

Foreword

The history of science, like that of all other fields of human endeavor, is marked by various fashions in thought which have predominated during certain periods. The human factor in the evolution of science is apparent throughout its many branches and can be traced in the development of chemistry, both pure and applied.

In the days of ancient Greece when manual experimentation was held in contempt, philosophers dreamed of four "elements" from which all matter supposedly stemmed: earth, fire, air, and water. Through the centuries which followed, a veil of mysticism and half-truth—pierced now and again at rare intervals by some scintillating intellect—shrouded man's wonder and curiosity about the world in which he lived. Gradually he began to toy with the merit of weighing ideas against observed facts. Slowly there dawned an appreciation of the inestimable value of well-planned, carefully executed, and critically interpreted experimentation. The curious witches' brews of the alchemist disappeared. The modern science of chemistry was brought forth.

By 1800 the new science of matter had gained a firm foundation in Dalton's atomic theory. Many of the more important elements were already recognized and a large number of compounds had been analyzed. An inexplicable difference, however, appeared to exist between compounds of mineral origin and those which were found in the vegetable and animal kingdoms. A considerable number of the former could be prepared in the laboratory, but the synthesis of the latter had thus far defied the chemist's ingenuity. It seemed that, somehow, nature had the power to construct in her laboratories of living matter compounds which, though they could be broken down by analytical methods, could not be built up by man. Thus there arose a division of chemistry into two branches, the one known as mineral, or inorganic, the other as organic in which some obscure "vital force" supposedly played an essential role in effecting synthesis. Bit by bit, doubt was cast upon the veracity of assuming that organic compounds must necessarily be associated with living, that is to say "organized," matter. Alcohol, urea, and acetic acid were produced in the laboratory. But these substances were at first thought to be exceptions which stood halfway between mineral bodies and compounds definitely known to be present in organized matter. At length, however, about the middle of the nineteenth century, masterly

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During the infancy of organic chemistry in the first half of the last century, an era when the elements were being discovered, when analytical methods were being developed, when empirical facts were being obtained without knowledge of their relationships to each other, and when the "vital force" theory waxed and waned, many suggestions were proposed for classifying and correlating this vast assembly of newly acquired knowledge in order to form a coherent basis for future scientific advance. The chaotic state of this field at that time can be judged by a quotation from Friedrich Wohler, eminent German chemist who is often inaccurately credited with the first organic chemical synthesis—an honor which rather belongs to the Englishman, Henry Hennell, who prepared alcohol from ethylene in 1826. In 1835 Wohler wrote Berzelius, "Organic chemistry just now is enough to drive one mad. It gives me the impression of a primeval tropical forest, full of the most remarkable things, a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter." Many theories were proposed and abandoned, but by 1840 sufficient order had emerged from the great mass of experimental detail—often not too exact—to make it possible for penetrating minds to divine that organic compounds must possess distinct molecular structures in which atoms of various elements are assembled in definite groupings. Once this idea was grasped, organic chemistry entered its adolescence—a period which was amazingly brief for the postulation of a few simple structural theories was so fruitful that as early as 1856 the English chemist, Sir William Henry Perkin, discovered mauve, obtained by the action of oxidizing agents on crude coal tar aniline. By that time the groundwork of the science had become well established and the chemistry and technology of coal tar dyes expanded rapidly. "Aniline colors" were numbered by the hundreds within two score years and, by the turn of the century, they had completely displaced natural alizarin from the madder crops of France and were menacing the natural indigo industry of the Orient.

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THE CHEMISTRY *of* COMMERCIAL PLASTICS

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TO
MY WIFE, GABRIELLE,
whose constant aid and encouragement have
made this work possible

Preface

For many years it has seemed to the author that increasing interest and enthusiasm in the ramifications of high polymers warranted publication of a text which would correlate scientific information in this domain with actual industrial practice. The need for such a book was evident when the writer first embarked upon research in this field. It became still further apparent when he was later engaged in university instruction and then in lecturing before many different types of audiences. The student had to be guided through the plant. The industrialist seeking to apply plastics in his business wished an introduction to the laboratory.

Since the time when this manuscript was begun, several authorities have published excellent and valuable books discussing various aspects of the plastics industry. Nevertheless, there still appears to be room for a critical analysis of the vast fund of information that was already more than voluminous in the days of Ellis' compendium and which has swollen to enormous proportions since then.

This text makes no pretense of being encyclopedic in the sense of Ellis. It does attempt to be selective with respect to information particularly pertinent to industrial practice. Regardless of theoretical interest, little or no consideration has been given to innumerable journal articles and patents which are not rather directly reflected in current commercial operations.

A word of explanation should be given concerning the abbreviated lists of literature references at the end of each chapter. They are by no means comprehensive, nor do they begin to cover the material consulted in the preparation of this book. Their purpose is two-fold: first, to suggest a few primary sources for additional reading; secondly—and still more important from an editorial viewpoint—to provide adequate means of acknowledging the large amount of graphical and tabular matter drawn from various publications.

The writing of this book was initiated and carried largely to completion while the author was occupied with an investigation of synthetic resins and plastics for the Pittsburgh Equitable Meter Company at Mellon Institute. It has been finished since his association with the Onyx Oil & Chemical Company.

To W. A. Hamor, Assistant Director of Mellon Institute, the author is grateful for his enthusiastic interest and invaluable suggestions throughout the preparation of the manuscript.

L. M. Van der Pyl, Chief Chemist of the Pittsburgh Equitable Meter Division, has redrawn from original publications all the graphs and several other diagrams used herein. He has adapted most of them in one way or another in order to enhance their presentation of data. He has also helped with some of the bibliographic work and has prepared a portion of the photographic material.

Many experts throughout the plastics industry have generously contributed assistance by painstakingly reviewing sections of the manuscript. For such help the author is indebted to Shailer L. Bass, Dow Corning Corp.; N. J. Beaber, Mellon Institute; Michael A. Brown, Jr., Monsanto Chemical Co.; W. C. Davis, American Cyanamid Co.; Albert L. Elder, Corn Products Refining Co.; C. H. Fisher and associates, Eastern Regional Research Laboratory; Harry L. Fisher, U. S. Industrial Chemicals, Inc.; Lyle M. Geiger, The Neville Co.; W. C. Goggin and associates, The Dow Chemical Co.; James K. Hunt and several associates, especially R. B. Akin, E. B. Cooper, V. A. Cosler, G. P. Hoff, A. F. Randolph, Charles H. Rutledge, E. W. Spanagel, F. V. Wemple, and L. G. Wise, E. I. du Pont de Nemours & Co.; K. B. Mathewson, Shawinigan Chemicals, Ltd.; F. M. Meigs and Margaret M. Flannery, General Aniline & Film Corp.; Cole P. Morgan, Vulcanized Rubber & Plastics Co.; George O. Morrison, Shawinigan Products Corp.; Frederick J. Myers and C. L. Levesque, The Resinous Products & Chemical Co.; Emil Ott and associates, Hercules Powder Co.; Richard W. Quarles, Mellon Institute; Alice G. Renfrew, Mellon Institute; Robert G. Ruark, Mellon Institute; J. Richter Salvesen, Marathon Corp.; L. T. Sandborn, Mellon Institute; George K. Scribner, Boonton Molding Co.; J. Kenson Simons and associates, Plaskon Division, L.-O.-F. Glass Co.; Allan K. Smith and Cyril D. Evans, Northern Regional Research Laboratory; Robert Steinman, Owens-Corning Fiberglas Corp.; H. R. Strohecker, Youngstown Welding & Engineering Co.; Harold E. Weaver, Mellon Institute; and Archie J. Weith, Bakelite Corp.

Many other kind friends have contributed valuable suggestions and information on specific subjects without which this book would have been less complete. Unfortunately, individual mention cannot be made of the large number of those who have supplied details on many different points, made available technical data on commercial products, and provided photographs. Kathleen Bronder of Mellon Institute has rendered much secretarial assistance in collecting this material.

The author is indebted to all owners of copyright matter which appears in this text. Permission for its use has been obtained in every case, both here and abroad. Sources are acknowledged through bibliographic references. Particular mention should be made of various publications of the

American Society for Testing Materials, as well as *Chemical and Metallurgical Engineering*, *Industrial and Engineering Chemistry*, the *Journal of the American Chemical Society*, and *Modern Plastics* from which a large amount of material has been drawn.

Finally, the author wishes to thank Messrs. F. M. Turner and G. G. Hawley, also Miss C. J. Loeffler and Miss J. M. Sternberg of the Reinhold Publishing Corporation for their cooperation in this work.

REGINALD L. WAKEMAN

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smelling, black, and sticky waste product, coal tar—bane of the gas-works engineer! Moreover, the brilliance of the products of the industry left no hint of their lowly origin and their ubiquitous colors enlivened even the most inexpensive articles of daily attire. The World War of 1914–1918 brought to America an acute realization of the importance of coal tar dyes. For the first time since their birth, their importation was arrested. The infant dyestuffs industry as it then existed in this country was unprepared to cope with such an emergency. It struggled valiantly, however, against great odds imposed upon it by the fundamental military exigencies of the epoch. The trials and vicissitudes of the long-suffering American public during the early days of the dyestuffs shortage, when laundering would often turn the black cotton stockings of those days a sickly green or gray, served only to emphasize the meteoric success of the American organic chemical industry which, by 1918, was filling domestic dye requirements with high grade products equal in quality to former imports.

Dyestuffs became the symbol of organic chemistry. Indeed, twenty years ago it was not uncommon to hear it said that all pioneering in this domain was over—that organic chemistry was no longer a virile science for no discoveries of fundamental importance had been made by its devotees since the brilliant *éclat* of the aniline dye industry!

Brief was the time during which pessimistic voices of this kind could gain audience. Not only then, but even before the birth of coal tar dyes and during the period of their pyrotechnic burst of splendor, the foundations were slowly being laid for a new period of glory for industrial organic chemistry, frequently—even if perhaps too enthusiastically—called the Age of Plastics!

Chapter 1

Introduction

Definitions

Plastics—around this word has raged many a philological battle; about its meaning has been fired many a polemical volley. As its use has developed in American industry, it now covers a large group of organic substances, either wholly or in part synthetic, which can be molded into coherent solid articles that retain their shape indefinitely at room temperature. In the stricter sense—which has been called by our British friends “An American perversion of the English language”—it refers specifically to molded articles which, themselves, are not plastic in the usual dictionary sense, but which are formed from materials that are plastic and hence moldable at some stage during the process of fabrication. From the chemist’s vantagepoint, this nicety of distinction between the fabricated article and the material from which it is made is often difficult to detect.

The essential components of all plastics are substances which possess resinous characteristics. Resins may be natural, partly synthetic, or wholly synthetic. For molding purposes they are often physically admixed with various fillers or plasticizers, according to type, and with other materials such as dyes and mold lubricants. There are other plastics besides those which are utilized in molded shapes. Many of them find use in the manufacture of sheets, filaments, textiles, adhesives, coating compositions, synthetic rubbers, and divers other commodities. Often a single kind of resin may be used in several of these products. It is becoming more and more difficult to erect a line of demarcation between molded plastics and the many other more or less shaped forms in which synthetic resins are employed.

The most conspicuous physical characteristic common to all resins is their lack of visible crystalline form. It is this lack of macro-crystallinity which accounts for many of their valuable properties, and therein also lies the reason for the scant progress made in this field during the early years of organic chemistry.

It has long been recognized that composite matter is made up either of definite chemical compounds or of physical mixtures. In a given compound, the elements are always combined in the same definite proportions regardless of the physical treatment which man may give it, such as

sieving, distilling, crystallizing, or levigating. In a mixture there are no necessary limitations on the proportions in which the elementary constituents can be mechanically admixed. Hence it is evident that, if the chemist is to obtain a fundamental insight into the nature of matter, he must work with pure compounds rather than mixtures. He must therefore first free whatever substance he is investigating from impurities. The laws of organic chemistry were established largely as a result of the analysis and study of the behavior of many carefully purified compounds. Two methods proved of particular value in carrying out these essential purifications: the one, distillation; the other, crystallization. It is not surprising that organic chemists became so preoccupied with methods of purification that nothing so filled them with chagrin as to carry out a reaction that resulted only in the production of a non-crystallizable and non-distillable resinous paste or tarry mass—which students to this day still call by the inglorious name of “gunk” or “goo.” Such uninviting products were anathema to the orthodox research chemist and were hastily abandoned.

We now know that there is an important difference between compounds which can be easily purified by distillation or crystallization and those which are resinous in nature. The difference is one of degree rather than kind. It lies in the number of atoms which are united in a single molecule of the compound. If only a few atoms are present, the molecule is small and the substance is a gas, a distillable liquid, or a solid which can usually be crystallized. Methane, known as marsh gas or fire damp, contains a total of but five atoms: one of carbon and four of hydrogen. Even the relatively complex crystalline glucoside indican, from which natural indigo is obtained, has a total of only forty-seven atoms of four different elements: carbon, hydrogen, oxygen, and nitrogen. On the other hand, where the individual molecules of a compound are constituted of a large number of atoms, the substance, either liquid or solid, cannot usually be distilled or crystallized in the form of visible crystals, although at times it may possess a sub-microscopic crystalline character detectable by x-ray diffraction patterns. It is exceedingly difficult to purify and is more or less resinous in character. All resins are composed of large molecules which may contain from a few score atoms to several hundred thousand. They are usually mixtures of many similar molecular species of varying weight. From a chemical viewpoint, the size of their molecules is the most distinguishing feature of the resinous components of plastics.

Natural Products Related to the Plastics Industry

In her laboratories of living matter in both the animal and vegetable kingdoms, nature is constantly building up many organic substances

which possess big molecules. Cellulose, universally present in plant tissue, and proteins which constitute the bulk of animal flesh, belong to this category. Even some of our mineral stores of vegetable origin, like coal and natural asphalt, show resinous characteristics. Ever since man first appeared upon this planet he has depended upon nature's high molecular weight products to supply him with the necessities of life. Leather, furs, and textiles made from various natural fibers such as cotton, flax, jute, and hemp, have clothed his body. Wood and straw have provided him with shelter. Coal and wood have warmed him. Meat and vegetables have given him sustenance. Sheets of cellulosic materials—paper during the past three centuries—have provided him with a medium upon which to inscribe his thoughts, transmit his knowledge, send messages of joy and sorrow. Substances constituted of big molecules make up the major part of all these gifts of Providence. In the development of modern plastics, the chemist has but taken a leaf from nature's notebook, sometimes simply modifying her products the better to suit his needs for certain purposes, sometimes imitating her synthesis of high molecular weight compounds, but in so doing making brand new substances of his own.

Asphalt and Pitch. Although plastics made by man from semi-synthetic resins have been known for scarcely a century and those derived from wholly synthetic resins were first produced commercially in 1910, yet the roots of the plastics industry reach back into the distant past for more than 5000 years of man's utilization of natural resins, gums, and asphalts. Indeed the discovery of natural materials of resinous character is lost in antiquity. Fossilized remains of plants and animals have been preserved for 250 centuries or more in the asphalt pits of Rancho-la-Brea near Los Angeles. Asphalt was used as an adhesive and cement even in prehistoric times. It was employed by the Sumerians more than 3000 years before Christ in the manufacture of mastic flooring—still an important use today. Ritualistic bathing pools built in ancient India were waterproofed with asphalt, while numerous references occur in the Bible to its use as a waterproofing agent and binder. Noah's ark, for instance, is supposed to have been protected thereby both within and without, while the Tower of Babel is thought to have been constructed with the use of an asphalt mortar. The Babylonians employed asphalt in paving their streets, an art subsequently lost and rediscovered only during the last century.

Methods of making more or less asphalt-like substances artificially are of far more recent origin. Although turpentine was known by the Greeks in the days of Herodotus or before, and although the naval stores industry was established in Scandinavia at an early date, yet the first

written mention of the large-scale production of wood pitch seems to have been made by Robert Boyle in his famous "Chemistra Scepticus." It was not until twenty years after that, in 1861, that two Englishmen, Joachim Becker and Henry Serles, patented their epochal discovery of the process for coking coal, thereby producing coal tar pitch.

Natural Resins. Asphalts and pitches are resinous materials. Both give rise to a conchoidal fracture upon breaking—often a simple way of deciding whether or not a substance is a resin. The products which are ordinarily called natural resins, however, and which find use especially in the varnish industry, are for the most part exudations of plants. They include both recent and fossil resins. Dammar, elemi, guaiacum, mastic, and rosin are typical recent resins; amber is fossil. Copal may be either recent or fossil. The word gum is often applied to some of these materials. It is common practice to speak of kauri gum or gum elemi, although the preferred usage of gum is restricted to complex materials of carbohydrate nature which are entirely different in composition from the natural resins. The true natural gums, like tragacanth and arabic, are soluble in water or at least swell therein. The natural resins are water-insoluble. Most of the latter have been used for many centuries in their countries of origin. Among those longest known in the West are amber, mastic, rosin, and Japan lac. Several that are now important, like New Zealand kauri, first mentioned in Captain Cook's diary for November 16, 1769, were not utilized in the Occident before the nineteenth century.

It would be an interesting study to trace the development of the technology of these natural resins through the ages. Some of them were used by the Egyptians in varnishing sarcophagi. Amber was known to the ancients, being used in the fabrication of both jewels and varnishes. Thales of Miletus, who lived about 600 B.C., is supposed to have discovered that, upon rubbing, this natural resin acquires the property of attracting particles of various light substances. Because of this characteristic, Queen Elizabeth's physician, William Gilbert, coined the word "electric" after the Greek for amber: *elektron*. It was in Gilbert's work, "De Magnete" (1600), that the terms electric force and electric attraction were first employed.

In our study of the history of the natural resins, we should be surprised, perhaps, by the role which they have played in the arts. Even before the Renaissance they were used by great painters and fabricators of stringed instruments. Their use in varnish was well known in the days when clocks were rare, so that we find recipes of the varnish cooker, like that of Jacobus de Tholetto, written in 1440, which instructs one to let the oil burn at the mouth of the kettle for the length of time required to say three paternosters. One often wonders if a similar combination of prayer and industry might not improve modern living!

The natural resin of greatest importance today is rosin, produced largely in this country and in France. The naval stores industry, which includes the manufacture of turpentine, rosin, and pine pitch, has been closely linked with the history of America. Indeed, in 1584 Philip Amados and Arthur Barlow referred to the oleo-resinous resources of the New World in a report to Sir Walter Raleigh. The production of turpentine and rosin was an important colonial industry. It began in 1608, an expedition being sent to the colony of Virginia expressly for this purpose. The industry was encouraged by both the Crown and the Colonies, as evidenced by Virginia's act of 1720 to favorize the making of tar in that province. It is of prime importance today in seven of the southern states from the Carolinas to Louisiana.

During the past two decades, America has learned much from the more scientific methods used by the French naval stores industry. The latter of necessity developed along conservational lines because the pine forests around Bordeaux are man-made and therefore limited in area. They are of recent origin, dating back only to 1803 when Brémontier began to plant pine trees in the Landes to fix shifting sands and eliminate disease from that formerly barren region.

Shellac. Although amber has been known many, many centuries and "gum" mastic is referred to by the Roman scientist, Pliny, shellac is of much later use. It is almost unique among resinous substances found in nature because it is of animal origin. The lac insect is mentioned in Sanskrit writings as early as 250 A.D., but the first known statement of its use in coating materials occurs in the *Ain-i-Akbari*, in 1590, where reference is made to a shellac varnish for the imperial palace. The Sanskrit refers to the "Lakshataru," or lac tree, now known botanically as *Butea frondosa*, one of the most important hosts to the cochineal-like insect, *Tachardia lacca*, which excretes the resinous deposit that hardens into shellac. It is an interesting fact that these millimeter-long orange-red insects were formerly valued more for the dye that could be obtained from them than for the shellac which they produce. If we should watch them closely we might be tempted to draw a parallel between today's civilization with its atomic bombs and these tiny creatures which manufacture their own death trap.

Although shellac has been used for centuries in varnishes, it became of significance as a molding composition only toward the end of the last century. Its use in conjunction with hard rubber had, to be sure, been contemplated by Nelson Goodyear in 1851 and spasmodic efforts were later made by others to utilize it as a moldable plastic, but it did not attract important attention until 1895 when Emil Berliner, after unsuccessfully trying to use hard rubber and nitrocellulose, found it satisfactory as a base for phonograph records. This use still accounts for

35–40 per cent of its domestic consumption in normal times. The amount utilized in this way is usually two or three times as much as the paint and varnish industry absorbs. The unique physical characteristics of shellac have allowed only one of the many newer plastics—"Vinylite"—to compete with it in record manufacture.

Early in the 20th century, shellac was introduced for the production of molded and laminated electrical insulation, and this use still ranks second in volume. Its low softening point, however, and its sensitivity to moisture made it imperative to find a substitute in the rapidly expanding electrical industry. Such a product was forthcoming in the phenol-formaldehyde resins, usually called the phenolics, sometimes the phenoplasts.

Until close to the middle of the last century, these various natural products and others like them were the only resins known. By the time that organic chemistry had cast off its swaddling clothes, natural resins were being used in such large amounts that the demand threatened to exhaust the supply. Moreover, the steady stream of technical advances resulting from the industrial revolution often demanded of a single constructional or decorative material various properties not coexistent in any known natural product. Such was the situation when the modern plastics industry was born. The history of this industry during the past century is a beautiful illustration of the application of scientific research of the highest caliber to the solution of difficult practical problems. Its early pages, even as its current chronicles, are filled with curious searchings after a motley group of things—from explosives and billiard balls to false teeth; from light bulb filaments to artificial silk and airplane wings.

Chapter 2

History of the Plastics Industry

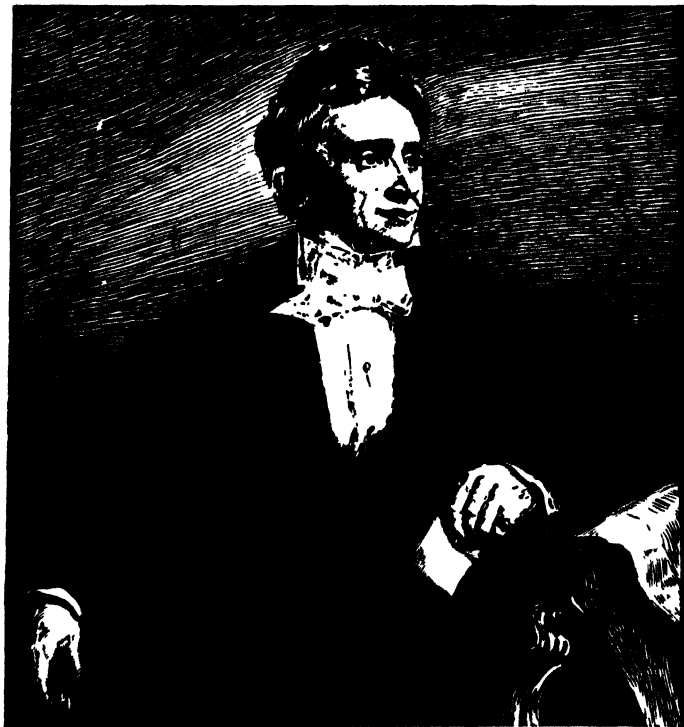
Rubber

The modern plastics industry had its inception in Charles Goodyear's discovery of the process of vulcanization in 1839. Rubber, or some similar substance like balata or gutta percha, occurs as the characteristic solid component of all aqueous, milk-like emulsions known as latex that are found widely distributed in the plant world. Latex-bearing plants which are common in North America are legion. Spurge, dandelion, golden rod, and milkweed are well-known examples. For various reasons, sometimes economic, sometimes chemical, the world's supply of natural rubber is obtained almost solely from a single botanical species, the tropical tree, *Hevea brasiliensis*, of South American origin, now cultivated on plantations throughout East Asia and in certain parts of Africa and South America as well.

Although 16th century descriptions of New Spain made casual reference to Indian games in which the players used a ball of elastic gum obtained from a native tree, the first observations of scientific significance relating to rubber were contained in a report of Charles-Marie de La Condamine submitted to the French Académie des Sciences in 1751. La Condamine was a member of an expedition sent to the Equator in 1735 for a geodetic survey. The expedition lasted several years, during which time La Condamine sent back from Ecuador samples of what he called caoutchouc, a Frenchified spelling of an expression meaning weeping tree in the language of the natives. He described its use by the Indians in the fabrication of such articles as water-resistant boots. The natives of Guiana called the tree Hevé, whence the botanical name *Hevea*, first applied in 1762 by the French botanist, Aublet, to *Hevea guyanensis*.

The rubber industry flourished for several years in England prior to the discovery of vulcanization. The first use of rubber was that from which it derived its English name and it is interesting to observe that the earliest known reference to this application was made by Joseph Priestley, famed English clergyman-chemist who removed to America in later life because of too fervent espousal of the cause of the French Revolution. In one of his writings, Priestley mentions "a substance excellently adapted

to the purpose of wiping from paper the marks of a black lead pencil.” Another Englishman, Charles Macintosh, developed a rubberized fabric used in raincoats which enjoyed considerable popularity, whence the still current name, *mackintosh*. Qwing to the less equable climate of the United States, most, if not all of the American firms which attempted to manufacture articles from crude rubber during the same period went into bankruptcy. The goods produced became brittle in winter, softened in



Courtesy the Goodyear Tire & Rubber Co., Inc.

Figure 1. Charles Goodyear. 1800–1860.

summer, and deteriorated badly upon exposure to air and sunlight, so that at least one New England firm which sold rubberized raincoats was kept as busy with damage suits as with manufacturing activities.

Soft Rubber. The process of vulcanization originated in the United States in 1839 with Charles Goodyear and was patented by him in 1844. Contrary to popular belief, his discovery was not the result of haphazard work and accidental luck, as, indeed, are very few scientific developments. It was the product of research—the outcome of several years of patient and persistent study of the properties of rubber and intelligent application

of knowledge acquired both by himself and his friends. As truth is stranger than fiction so, indeed, is the story of Goodyear's trials and tribulations! Because of his devotion to the study of rubber he incurred debts that he could not pay, an unhappy circumstance for which he atoned in prison. While in jail, his friends attempted to dissuade him from his experimental ardor, but in vain. At long last, after many troubles, he hit upon the idea of reacting rubber with sulfur in the presence of litharge and his patience was rewarded by successful conversion of the raw substance into a stronger, yet elastic material far more resistant to heat and cold.

In 1842, samples of Goodyear's cured rubber were taken to England by a friend who sought to interest British capital in the discovery. For several years prior to that time, Thomas Hancock, inventor of rubber mastication, had been manufacturing articles from crude rubber in London. He was well aware of the limitations of his products, but did not know how to overcome them. Goodyear's samples came to his attention through a friend named Brockedon, and he at once set about to discover the secret of what had been done to the rubber to change its properties so radically. In the following year he duplicated Goodyear's work and obtained a patent in 1843. It was Hancock's friend, Brockedon, who suggested the term vulcanization because of the association of the Roman god with fire and brimstone.

Hard Rubber. Twelve years after Charles Goodyear discovered the process of vulcanization, a younger brother, Nelson, not to be outdone by his elder, found that by incorporating a much higher percentage of sulfur in rubber, its softness and elasticity disappeared and hard rubber, called ebonite because of its resemblance to ebony, resulted. On May 6, 1851, Nelson Goodyear was granted the first hard rubber patent and during the same year, Goodyear interests displayed at the Crystal Palace Exhibition in London a room in which all of the furniture was made of rubber, including ebonite chairs and bureaus.

Hard rubber rapidly increased in importance, becoming of invaluable assistance to the development of the infant telegraph and later the telephone. It was soon an important factor in the production of buttons and druggists' sundries. Even as early as 1851, the India Rubber Comb Company of New York was operating a factory at Williamsburg, Long Island.

Cellulose Nitrate

In 1846 an important contribution to rubber technology was made by the Englishman, Alexander Parkes, who developed the sulfur chloride method of cold vulcanization. About ten years afterwards he also began

to experiment with a second type of semi-synthetic, nitrocellulose. During the subsequent decade he worked out a rather unsatisfactory way of making shaped objects from this material. Owing to the fact that he prepared his plastics by evaporation of considerable volumes of solvent, his costs of manufacture were very high. In order to obtain financial backing, he understated them and, in 1867, was forced to suspend operations because of ill-advised attempts to cut expenses by cheapening his products, by failing to control quality, and by insufficiently seasoning his goods to remove volatile solvent prior to sale. Following Parkes' business failure, one of his associates, Spill, produced a more successful nitrocellulose plastic, calling it "cotton xyloidine" or "xylonite." Spill established the British Xylonite Company, Ltd., and it remains today one of the principal British producers of plastics, not only nitrocellulosic, but others also.

Neither of these two Englishmen had discovered nitrocellulose. Already well-known when they began their work, it was first made in 1838 by the French chemist, Pelouze, who had nitrated paper. Even five years before him, another Frenchman, Braconnot, had nitrated starch and obtained a related substance which he called "xyloidine," a name later adopted by Spill, as we have just seen.

During the years which followed the early discoveries of Braconnot and Pelouze many investigators studied the properties of nitrocellulose. Schoenbein, at the University of Basel in Switzerland, worked with it in 1845 and 1846. He appears to have been the first to recognize its military importance—possibly because of his Teutonic origin—although it was not until fifty years later that careful control of manufacturing operations made possible the adoption of cordite, or its equivalent, by the great powers.

In 1851, nitrocellulose was utilized for the manufacture of photographic film by the Englishman, Scott Archer, while three years earlier collodion, a nitrocellulose solution, had been introduced for medical use by the Bostonian physicians, J. Parker Maynard and S. L. Bigelow.

"Celluloid." In 1863 the American firm of Phelan and Collender offered a \$10,000 prize to anyone who would assign them patent rights to a satisfactory process for manufacturing billiard balls without the use of solid ivory. An advertisement of this offer came to the attention of an enterprising and ingenious Albany printer, John Wesley Hyatt, who at once set about to win the award. For several years he experimented with shredded paper, ivory dust, and miscellaneous other powders which he bonded together with natural gums and resins. The experiments which he carried out led him to perfect methods of molding his compositions under heat and pressure.

In 1868 he began to use nitrocellulose in his operations. This material suggested itself to him when he discovered the dried residue deposited on a cupboard shelf by evaporation of solvent from an upset bottle of colodion which he was accustomed to keep on hand for protecting chapped finger-tips. He was unaware of any prior experimentation in this field by either Parkes or Spill and, because of the former's business failure, he is usually credited with originating nitrocellulose plastics.

In 1869 John's brother, Isaiah, an Illinois editor, joined him and together they developed methods of manufacturing nitrocellulose plastics by using camphor as the principal solvent, an operation made possible



Figure 2. John Wesley Hyatt. 1837-1920.

Courtesy Celanese Plastics Corp.

by appropriate application of heat and pressure. This obviated the use of large volumes of expensive solvents which otherwise had to be removed after molding—the stumbling block of Parkes' earlier work. At the same time, use of camphor improved the physical properties of the finished product.

In 1870, the Albany Dental Plate Company was organized to manufacture colored nitrocellulose plastic for dentures. The early days of the company were troubled by short-lived litigation with the newly-formed American Zylonite Company that began operating Spill's American patents under license. Spill's patent position was weak, however, and the fight soon ended by the Hyatt Brothers' absorption of their competitor. The potentialities of molding numerous light and bright-colored objects from Hyatt's plastic—which the ex-editor named "Celluloid," meaning cellulose-like—were apparent almost from the beginning. In 1873 a group

of New Yorkers invested capital in the organization, then known as the Celluloid Manufacturing Company, and a new factory was built in Newark. In 1890 it underwent business consolidation and reorganization under the name of The Celluloid Company. It has operated since that time in Newark. Recently it was consolidated with the Celanese Corporation and is now known as the Celanese Plastics Corporation.

Nitro Silk. The expanding utility of nitrocellulose was by no means confined to the realms of explosives, photographic film, collodion, and molded articles. It was also the first material successfully used in the manufacture of artificial silk. This industry dates back to a sealed document deposited in 1884 with the French Académie des Sciences by the chemist, Count Hilaire de Chardonnet, and to a patent granted the same gentleman on November 17th of that year. It should be noted, however, that during the preceding year, an Englishman, J. W. Swan, had obtained British patent protection for a process of spinning a solution of cellulose nitrate in glacial acetic acid, the object being preparation of threads which could be carbonized for use as incandescent lamp filaments. A number of other Englishmen, including the electrician, Weston, were also granted similar patents at about the same time. Swan prepared a limited amount of artificial silk at a later date. Although samples of Chardonnet silk exhibited at the Paris Exposition of 1889 enjoyed enthusiastic popular acclaim, it was not until some ten years later that it became a significant commercial article. Because of the hazardous flammability of nitrocellulose, methods of denitration had to be developed and, with this improvement, regenerated cellulose filaments prepared from spun nitrocellulose remained one of the most important artificial silks until after the World War of 1914–1918. During the last two decades, "nitro silk" has become practically extinct, having been displaced largely by viscose rayon. American production finally ceased in 1934.

Airplane Dopes. Nitrocellulose has had a curious career. It has often served as an indispensable pioneer material for important technologic advances, but in several instances it has turned out to be a stop-gap used only for a little while until more suitable products could be evolved. Artificial silk is one illustration; there are several others. In the early days of the airplane, fabric wings were doped with nitrocellulose (pyroxylin) solutions. This application was a tremendous boon to the development of aviation, for the dope not only waterproofed the fabric, preventing substantial fluctuations in weight due to absorption of moisture over relatively large wing surfaces, but it also tautened it, thus improving the aerodynamic characteristics of the machine.

When the First World War broke out, however, the Allies soon found

it necessary to replace nitrocellulose with a less flammable dope for military planes. Cellulose acetate was the answer to this situation. Both acetate silk and acetate molded plastics were outgrowths of this development.

Automobile Lacquers. Pyroxylin solutions similar to those used for airplane dopes were first employed by Wilson and Storey in 1882 for the fabrication of artificial leather. Considerable volumes of nitrate solution have been used for this purpose since that time. Both artificial leather dressings and airplane dopes require the use of thick, viscous solutions, but the formulation of lacquers and enamels necessitates the use of a resin base of such physical characteristics that relatively concentrated solutions will possess sufficiently low viscosity to flow freely under the brush or spray readily with a gun. For many years only slow progress was made in the evolution of technical procedures for the preparation of nitrocellulose of standardized low viscosity characteristics. When, at last, such pyroxylin could be produced, the trade was faced with the requirement of large volumes of special solvents for lacquer formulation. Prior to World War I, the only satisfactory solvent for this purpose was derived from fusel oil, a by-product of the fermentation industry. The available amount of this material was limited and its price rose with demand, so that industrial applications of nitrocellulose lacquers were curtailed by both cost and availability of solvent. During the War, acetone was imperatively needed for military purposes in order to remove dangerous impurities from cordite-grade nitrocellulose. This fact caused the development of the Fernbach-Weizmann fermentation method for producing it from corn starch. A by-product of this process is butyl alcohol, a substance for which there was then no demand. Huge stocks were accumulated during the war, awaiting the time when attention could be devoted to its utilization. After the close of hostilities, it was found that butyl alcohol could be converted to an excellent pyroxylin solvent: butyl acetate. This initial discovery and subsequent development of other satisfactory solvents, coupled with the evolution of ways of making low viscosity nitrocellulose, resulted in the astonishing increase of pyroxylin lacquer production from 500,061 gallons in 1919 to 12,980,400 gallons seven years later. Most of this quick-drying lacquer was used in automobile finishing—an operation which had formerly been a serious bottleneck, elimination of which greatly facilitated expansion of motor car manufacture.

Safety Glass. Nitrocellulose has served the automotive industry in another important capacity besides that of lacquer base, namely, as the first successful interlayer in safety glass. The earliest attempt to make a shatterproof glass was carried out in 1901 by the Englishman, Wood,

who used a gelatin interlayer. Ten years later the Frenchman, Benedictus, commercialized a product of this kind on a limited scale. Fifteen years more elapsed before sandwich glass, made by cementing two pieces of glass together with an intermediate sheet of nitrocellulose, became a practical reality for automobiles. Many an individual owes his life to this happy combination of glass and plastic. For several years, nitrocellulose ruled with undisputed sway in this realm of technology, but it possessed certain undesirable properties which chemists soon set about to overcome. Most serious among its flaws was a susceptibility to discoloration in sunlight. This trouble could be largely eliminated by incorporating iron oxide in the chemical composition of the glass which, thus made, absorbed much of the ultraviolet light that caused the nitrate to discolor. Glass which contained sufficient iron oxide, however, possessed an undesirable greenish tint. To overcome this and other limitations of nitrate safety glass, cellulose acetate was developed as an interlayer. Finally, during the past ten years, still another purely synthetic plastic of the vinal type has largely displaced cellulose acetate because of superior safety characteristics at low temperatures.

Cellulose Acetate

Although cellulose acetate no longer holds first place in safety glass production, its consumption has increased annually by leaps and bounds because of expansion of its use in artificial silk and molded plastics. The career of this semi-synthetic, like that of nitrocellulose, is an absorbing tale of modern science and technology.

Cellulose acetate was first made in the laboratory of Paul Schutzenberger, an Alsatian professor at the Sorbonne. He described it in a communication to the Académie des Sciences in 1865, but like many other products of today's industry, his discovery lay dormant in the ponderous tomes of the *Comptes rendus* for many years before any practical application was contemplated. A few years later another Frenchman, Franchimont, made an important improvement in the preparative method which paved the way for later industrial development. Technologic application of this material was first forecast in a British patent granted in 1894 to the Englishmen, Cross and Bevan. Little progress was realized in its early industrial development, however, for several reasons: (1) The product was soluble only in relatively toxic and expensive chlorinated solvents like chloroform. (2) It was extremely difficult to dye. (3) It required the use of rather costly acetic anhydride for its production.—The first and most serious of these difficulties was overcome by an American, G. W. Miles, who between 1903 and 1905 patented a simple process for modifying the chemical nature of cellulose acetate in such a manner

as to alter its solubility characteristics so that it could be dissolved in relatively cheap and non-toxic solvents like acetone. This modified type of acetate could also be dyed with a few basic colors, although dyeing problems still presented serious obstacles to its application.

Various samples of acetate silk, such as the German product "Celestron," are mentioned in the literature between 1898 and 1910, but they did not result in important commercialization. In the United States, the Lustron Company of Boston pioneered large-scale production of acetate silk under patents granted to A. D. Little, W. H. Walker, and H. S. Mork between 1902 and 1908. The Bayer Company in Germany developed commercial manufacture for other purposes, using the trade name "Cellit."

Two Swiss brothers, Camille and Henri Dreyfus, carried out an experimental study of cellulose acetate during the early years of this century and, between 1910 and 1913, began its manufacture on a small scale at Basel. When the First World War broke out, the British Government requested them to come to England in order to assist in the development of nonflammable airplane dope and in 1916 the British Cellulose and Chemical Manufacturing Co., Ltd., was established with government aid. This concern supplied a vast amount of dope to the Allies during the War. After the Armistice it was necessary to readjust operations to peace-time pursuits. The large demand for dope being no longer existent, outlets for acetate were sought in the fields of photographic film, molded plastics, and artificial silk. The last proved the most promising. The product was given the trade name "Celanese" and the name of the company was subsequently changed to British Celanese, Ltd. Many affiliated companies have been established throughout the world, including America, for the manufacture of acetate yarn by Celanese processes. Numerous other firms have entered this field in recent years.

Dyeing difficulties at first limited the utilization of acetate silk, but two different ways of solving this problem were soon found. First, a new class of rather complicated water-soluble dyes (called "Ionamines") was developed. Their solubility could be conveniently terminated at the moment of application. Second, dyes which are insoluble in water but soluble in oil were used in aqueous suspensions produced with the aid of any good emulsifier—turkey red oil at first (whence the name "S.R.A. dyes," from sulfonated ricinoleic acid), later many other surface-active agents, even soap. Cellulose acetate, being more like oil than water, tends to extract these oil-soluble dyes from their aqueous media. The second solution to the dyeing problem is obviously quite simple and is the one most widely used today.

In 1927, by agreement between the Celanese Corporation and the Celluloid Company, American production of acetate in sheet, rod, and tube form similar to "Celluloid" was begun, the product being known under the trade name "Lumarith." Two years later, acetate molding powders appeared. Several other American firms have since entered this field, while the development of injection molding methods has greatly expanded the utility of acetate molding powders. Chemical inventions have reduced the cost of intermediate acetic anhydride to a fraction of its former value so that, by 1940, 175,000,000 pounds of cellulose acetate were manufactured in the United States for conversion into artificial silk, safety film, transparent sheet material for packaging purposes, and molded plastics ranging in applications from oil cans to automobile steering wheels.

Regenerated Cellulose

While this development of acetate was in progress, other important plastics were also born of cellulose. Various ways were discovered for manufacturing solutions of cellulose derivatives which, by treatment with suitable reagents, could be re-precipitated as so-called "regenerated cellulose."

Viscose Rayon. One of the earliest of such methods involved the use of a complex ammoniacal solution of a copper salt, known as Schweitzer's reagent, and although the product was somewhat brittle when dry and was rather flimsy when wet, it was used for several years on the Continent as artificial silk called "Glanzstoff." (Viscose silk was later manufactured under this name, also.) It enjoyed popularity because of its remarkable sheen until newer cellulosic products displaced it from the market. Most important among regenerated forms of cellulose, however, is viscose silk, the common variety of today's rayon. It is produced by an interesting series of chemical reactions in which a complicated water-soluble sulfur derivative of cellulose—viscose, is first made and then spun from aqueous solution into a precipitating bath. It was developed by three Englishmen, Charles F. Cross, Edward J. Bevan, and Clayton Beadle, to whom a joint patent for its production was issued in 1892.

Cellophane. Sixteen years later, in 1908, Brandenberger of Neuilly-sur-Seine, working at the Blanchisserie et Teinturerie de Thaon-les-Vosges, France, produced transparent films of cellulose regenerated from viscose. Within four years' time, films of "Cellophane" ("cello" from cellulose; "phane" meaning shine) were marketed successfully on a small scale in France. Several years later the du Pont Company purchased both patent rights and trade-mark, whereupon "Cellophane" rapidly

became a household by-word in this country. Du Pont later lost its rights to the use of "Cellophane" as a trade-mark.

Casein Plastics

While these developments in cellulosic derivatives were occurring, the search was going on for other plastics to supplement natural products. Casein plastics from milk were developed in 1897, being the result of a German desire to produce white slates for school children. The product, placed on the market under the trade name "Galalith" (from the Greek, meaning milk stone), achieved particular success in Europe in the fabrication of jewelry and buttons. It was not made in this country until about 1919 and has been used here almost exclusively for the manufacture of buttons and buckles. Some of the applications which were possible in Europe are impractical here because of the less equable climatic conditions of the United States, a cause of serious deterioration of this plastic. Artificial wool, more recently developed in Italy and now produced in many other countries, including the United States, has broadened the utility of casein plastics.

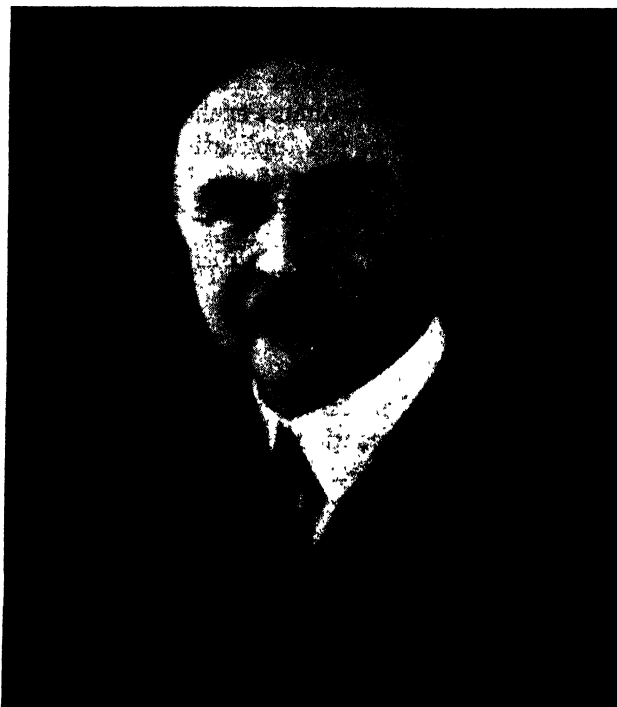
Phenoplasts. "Bakelite"

The phenolics were the first industrial plastics of purely synthetic origin, being produced by the reaction of relatively simple, low molecular weight chemicals of commerce, namely phenol and formaldehyde. Among the true synthetics, they are not only the oldest, but they are still the most versatile and the most widely used in molding applications. It is gratifying to note that both their discovery and their technical development have been accomplished by the genius of American science and industry.

Eminent chemists had obtained resinous masses from phenol and formaldehyde as early as 1872, but little attention was then paid to a product which could not be crystallized or distilled. In the early days of the present century, a number of investigators, both in this country and abroad, interested themselves in possible technologic uses of such products, but no commercially applicable results were obtained prior to Baekeland's brilliant work. In 1905 Dr. Leo Hendrik Baekeland, a Belgian chemist who had come to this country as a young man and was already well-known because of his invention of "Velox" photographic paper, began to study the condensation of phenol with formaldehyde. He possessed a high degree of business acumen as well as chemical ability and was quick to foresee the important role which his resinous products might play industrially. From his private laboratory in Yonkers, New York, soon came the world's first synthetic plastics.

In 1907, small-scale production of "Bakelite" was under way at Yonkers, and three years later the General Bakelite Company was organized to produce phenolic resins which, at first, were consumed largely by the electrical industry.

A humorous tale of one of the earliest episodes in the history of the General Bakelite Company is entertainingly told in the Silver Anniversary Number of the "Bakelite Review."



Courtesy Underwood & Underwood

Figure 3. Leo Hendrik Baekeland. 1863-1944.

"All through the day in a small leased building at Perth Amboy, N. J., a handful of men strove patiently to complete their first big order. When darkness approached, their only light was an oil lantern, but with their improvised machinery they had nearly completed their work. It was time to start the second-hand steam engine which was to turn the stirrer in the 600-gallon still. Every minute counted, for the chemical reaction might get out of control. Precious seconds passed while they hitched the steam engine to the still. More, before the engine made but half a revolution, and then failed to function.

"Even then, all was not lost. The engine disconnected, a dozen hands turned the stirrer for a solid hour, while others passed buckets of alcohol to a man on a shaky platform who poured it into the still.

"At last, by dint of main strength, the awkward job was completed amid great sighs of relief . . . in the morning General Bakelite Company's first 'huge' shipment of eight barrels of varnish would be on its way to Westinghouse Electric and Manufacturing Company, which was pioneering in Bakelite Laminated production.

"Suddenly, without a word to anyone, a 'bright' young chemist, who had observed all operations with inquisitive interest, picked up the lantern, jumped to the platform, opened the manhole door of the still, and stuck the lantern into the opening to see the results. The inevitable happened—one grand boom! The alcohol vapor had exploded—fortunately without doing serious personal injury, for the chemist had not put his head well over the manhole. The flames, however, made short work of his shock of curly hair."

Soon after Baekeland's early work, similar resins marketed respectively as "Condensite" and "Redmanol" were developed by J. W. Aylsworth, chemical consultant for Thomas Edison, and by Dr. L. V. Redman and his associates, Weith and Brock, who were engaged at the University of Kansas in the organization which since that time has become Mellon Institute of Industrial Research in Pittsburgh. The latter products were originally evolved to serve as a furniture varnish, especially for brass beds.

After considerable litigation, the Redmanol and Condensite Companies finally merged with the Bakelite Corporation in 1922. For a few years this organization enjoyed a monopoly of the phenolic re-in field, but when Baekeland's basic patents began to expire in 1926, other companies started operation, until today some thirty American firms are engaged in the manufacture of phenoplasts either for sale or for their own consumption.

Coumarone Resins

Industrial synthesis of an entirely different type of resin, the paracoumarones, also derived from coal tar, had its inception in the work of two German scientists, Kraemer and Spilker in 1890. These resins were manufactured in Germany during World War I and were used to some extent as a substitute for rosin in paints and varnishes. Their early acceptance in this country was impeded by difficulty in obtaining products of consistent uniformity, but by 1919 such troubles had been largely overcome and production was begun by the Barrett Company under the trade name "Cumar." Ten years later the Neville Company began their

manufacture, while still ten years after them a third concern, the Pennsylvania Industrial Chemical Corp. entered the field.

Alkyd Resins

We have already followed the development of cellulose nitrate in automobile lacquers. In their formulation, natural resins were used in appreciable amounts as essential adducts, especially for the purpose of improving gloss and adhesion. Scarcely had these coating materials established a place for themselves in the industry when it was found that some of the purely synthetic resins developed since 1900 could also be used as adjuncts to nitrocellulose. Phenolics of the "Bakelite" type were the only 100 per cent synthetic resins manufactured on a large scale when nitrocellulose lacquers were first introduced, but a number of other types had been discovered and partially investigated. Among the latter were the so-called alkyds. They were found to be especially suitable for lacquer formulation in combination with pyroxylin.

The Englishman, Watson Smith, is generally credited with their discovery which he related in an instructive paper presented before the Society of Chemical Industry in 1901. Although he failed to see the commercial utility of his chemical invention, he gave such a surprisingly accurate picture of the resinous character of the reaction product of glycerol and phthalic anhydride that, in the discussion which followed, its analogy to cellulose and nitrocellulose was mentioned, although at that date little was known concerning the chemistry of large molecules. Smith's only suggestion of an application for his product was a remark that he had found it a suitable cement for use with glass and earthenware.

His work was soon continued by chemists at the General Electric Company in this country, to whom several basic patents were issued in 1914. The cost of intermediates delayed exploitation of these patents until methods for the catalytic oxidation of coal tar hydrocarbons were developed. About 1926, alkyds were placed on the market by the General Electric Company under the trade name "Glyptal," a word apparently derived from the two most important components of these resins, glycerol and phthalic anhydride. The more important products of this nature were modified with natural resins or with non-drying vegetable oil acids, because such materials were found to be compatible with nitrocellulose and could be used to advantage in the formulation of pyroxylin lacquers. A most significant technologic advance was made when it was discovered that on modification with drying oils like linseed or tung oil, alkyds would air dry even more rapidly than the oils from which they were made. Moreover, nitrocellulose could, if desired, be

completely omitted in their formulation. Thus, pyroxylin lacquers were first made commercially practicable through the availability of inexpensive solvents from by-product butyl alcohol; then coating materials were developed in which modified alkyds played an essential role; and, finally, lacquers were evolved in which drying oil modified alkyds constituted the entire resin content. This unique series of developments leading to modern automobile and refrigerator lacquers is another instance of a field in which nitrocellulose did pioneer work where other resins later became preeminent.

The plastics which have been discussed in this chapter constitute those of commercial importance before 1925. Since then others have appeared upon the market in great profusion, exhibiting a wide range of properties which adapt them to an amazing variety of applications. Some of them, although new to commerce, have been known to scientists for many years. Polystyrene, for example, was first prepared in the laboratory in 1839, but not until 1937 did it become generally available in this country. Others, like nylon, are new in every respect, being entirely unknown to chemists even a decade ago. Subsequent chapters will give a brief historical account of many of these newer materials.

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Chapter 3

Raw Materials of the Plastics Industry

Ebonite and "Celluloid," the first man-made plastics, were the result of chemical modification of two natural vegetable products of high molecular weight: rubber and cellulose. Nature had already carried out by far the more difficult part of their syntheses before the chemist took over and carried on. Such plastics are known as semi-synthetics. In recent years many more semi-synthetic resins have been developed from these and other natural materials of high molecular weight like casein, lignin, and soybean protein.

With the advent of "Bakelite" came the first purely synthetic plastics made from low molecular weight, relatively simple chemicals of commerce—phenol and formaldehyde in this instance. In such syntheses the chemist starts with small molecules and builds up large ones. Indeed, if he wished, he could prepare phenolic resins from the elements—carbon, hydrogen, and oxygen—as he does in the case of some of the newer plastics. Cost, alone, deters him from making phenoplasts this way.

The last twenty years have seen the introduction of many purely synthetic resins made entirely from products of chemical industry. The alkyds, methacrylates, polyamides, and vinyl resins are but a few which have come in their entirety from the chemist's art.

At the present time, industrial honors are shared about evenly by semi-synthetics and synthetics. Both classes are constantly growing in volume of sales, diversity of applications, and multiplicity of types.

The principal raw materials from which synthetic resins and plastics are made are, therefore, of two different categories depending on whether the products are synthetic or semi-synthetic. For synthetics, coal tar, petroleum, coke, limestone, salt, natural gas, air, and water constitute the major sources. Sometimes added to these are turpentine, rosin, and drying oils. For semi-synthetics, cellulose, lignin, rubber, and various proteins from milk, soybeans, and corn make up the most important raw materials. With the single important exception of rubber, practically all of the raw materials for both synthetic and semi-synthetic plastics are of domestic origin, or can readily be produced in this country if desired. Furthermore, the amounts of these raw materials available here

are in almost every instance considerably in excess of the quantities consumed. Hence, the potential production of plastics is limited by demand and by manufacturing facilities rather than by shortages of fundamental raw materials.

In this chapter we shall examine in a general way some of the relationships which exist between the various raw materials just mentioned and the plastics made from them. We shall deal first with source materials of the purely synthetic resins.

Modern advertising tends to stress the origin of consumer goods. Articles ranging from nylon stockings to "Lucite" surgical instruments are said to be derived from coal, air, and water. "Ameripol" and other synthetic rubbers have been proclaimed to originate with petroleum, natural gas, and air, while "Krene" bath curtains have been tagged as products of natural gas, coke, air, salt, and limestone. The accuracy of these statements is beyond reproof, but to the layman their brevity conjures up the image of a chemist dashing downstairs to his coal bin, grabbing a shovel of coal and a bucket of water and then, by some miraculous legerdemain, returning to milady's chamber with a new silk negligee! Great is the complexity of the metamorphoses through which coal, air, and water pass before they finally emerge as plastics—often called "the gems of modern research" or "industry's glamour girl."

COAL

Carbonization

When coal is heated in the absence of air it decomposes. The principal product is carbon in the form of coke, but a considerable quantity of volatile matter is driven off during formation of the latter. This process is not a simple separation of coke from distillable components of the original coal, for the chemicals found in the distillate are not present as such before heating. It is a destructive distillation which involves far-reaching decomposition of the complex compounds that make up the coal substance.

The volatile matter is partly gaseous, partly liquid, partly solid. The products vary in chemical nature according to the conditions of carbonization. They are separated by diverse processes of condensation, scrubbing, and distillation into coal gas; ammoniacal water containing ammonium sulfate and other salts; benzol or light oil, made up largely of benzene and related hydrocarbons; and coal tar.

Huge volumes of coke are consumed in making iron and steel. In operations of this industry, coke is the desired product and incidental volatiles are either recovered as by-products or, in the case of beehive coking, they

are lost. The manufactured gas industry also carbonizes large volumes of coal in order to obtain gas for heating, illuminating, and industrial purposes. In this instance coke is a by-product as are also tar and other oily condensates.

Coal tar and light oil are important raw materials for the chemical industry. We have just seen that they are by-products of both the steel and gas industries and may or may not be recovered for sale. Beehive coking, which recovers neither, is a wasteful operation. Although it gives an excellent coke for metallurgical purposes, it had been gradually giving place to by-product recovery processes before World War II. Imperative military demands for coke, however, caused a resurgence of beehive operations during the recent war. By no means all of the coal tar produced in this country even from by-product recovery processes is utilized by chemical industry. In normal years, approximately half of it is burned as fuel at the source, or at nearby steel mills. Hence the actual production of coal tar chemicals is only a fraction of the potential volume which could be obtained from tar recovered but not distilled and this, in turn, is but a fraction of what would be available were all coking operations of the by-product recovery type.

Figure 4 shows the manifold ways in which coal tar and light oil serve as raw materials for the plastics industry.

Coal tar is a complex mixture, a veritable gold mine of organic chemicals, many of which, however, are present to the extent of only a fraction of one per cent and either cannot be separated economically by current methods or are not in demand by chemical industry. Over two hundred different compounds have been tabulated as components of coal tar and this list is probably conservative. Among all these products, benzene, toluene, xylene, certain mixed fractions of solvent naphtha, naphthalene, phenol, the cresylic acids, and pyridine and its analogs are easiest to obtain in a pure state and are in greatest demand. They are separated by means of suitable combinations of distillation and extraction with alkalies or acids. Recently some tar has been stripped without completely distilling it, in order to obtain the more desirable constituents. This practice, known as topping, was first introduced in 1936.

Manufacturers of plastics draw upon coal distillates for several important intermediates, especially benzene, phenol, the cresylic acids, naphthalene, and the coumarone-indene content of solvent naphtha cuts.

Tar Acids

So-called tar acids, consisting chiefly of phenol, cresols, and xylenols, are separated from coal tar distillates by extraction with alkali. Phenol obtained in this way is called "natural." Only a portion of the natural

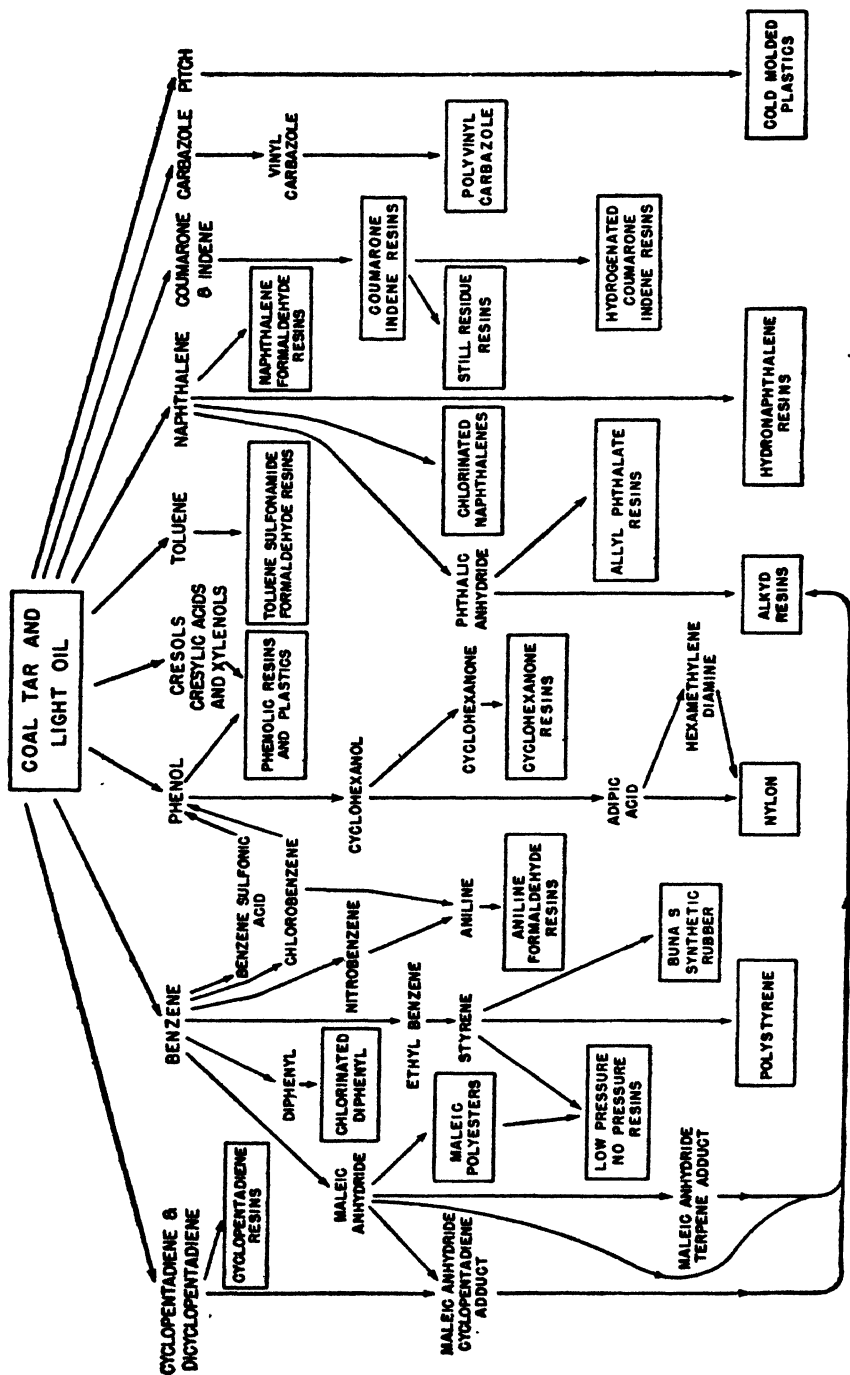


Figure 4. Derivation of synthetic resins and plastics from coal tar and light oil.

phenol which could be extracted from the coal tar recovered in domestic by-product coking operations is actually obtained. In the typical pre-war year of 1936, for example, less than 25 per cent of the estimated tar acid content of domestic coal tar production was recovered. Natural tar acids are obtained in the approximate ratio of 50 per cent phenol and 50 per cent cresols and mixed cresylic acids. Considerably more phenol is produced by synthesis from benzene than by direct separation from coal tar.

Three different methods are employed industrially for converting benzene to phenol, all of them being worked in this country. The oldest was initiated during World War I and involves sulfonation of benzene with concentrated sulfuric acid followed by fusion with caustic soda. In 1918, 107,000,000 pounds of phenol, synthetic and natural, were produced in America. Cessation of hostilities caused an immediate slump in demand and synthetic production was suspended until 1923 when it was again begun by four concerns. In 1926 the Dow Chemical Company started operation of a new and relatively inexpensive way of making phenol. Intermediate chlorination of benzene was followed by heating with caustic soda under pressure, a method peculiarly adapted to Dow's operations because of availability of chlorine. In 1939, a third synthetic phenol process began operation in this country, being worked by Durez Plastics and Chemicals, Inc., under patents of German origin. Fundamentally, the Durez process is a partial oxidation of benzene by means of atmospheric oxygen, although it is necessarily effected by a round-about procedure.

During the ten year period, 1933-1943, about 66 per cent of the total American production of phenol, both natural and synthetic, was consumed in the manufacture of synthetic resins of the phenolic type. The applications of these products are legion and vary from molded and laminated articles to paints, lacquers, and coated cloth. A smaller, but appreciable volume of phenol is also converted into adipic acid and hexamethylene diamine used in the manufacture of nylon. Both phenol and cresols are employed in the manufacture of several important plasticizers for synthetic and semi-synthetic resins.

Dicarboxylic Acids

The alkyds, another group of large volume synthetic resins, also depend upon coal tar for raw materials. These products, used largely in the formulation of paints, varnishes, and lacquers, are derived from dibasic acids or their anhydrides, among which phthalic anhydride is most important and maleic anhydride next. Both of these compounds are manufactured by catalytic oxidation of coal tar hydrocarbons: naphthalene and benzene,

respectively. Neither compound was an article of any commercial importance prior to World War I, although small amounts of phthalic anhydride were then sold at several dollars a pound for use in the manufacture of limited quantities of a few high-priced dyestuffs. In 1918, this chemical cost \$2.85 per pound. Today it sells at about 13 cents and is the cheapest acid of the aromatic series, being even less expensive than time-honored benzoic acid which, oddly enough, is economically made from it today. The discovery of catalytic oxidation methods accounts for this phenomenal drop in price.

American industry is indebted to two government chemists, Gibbs and Conover, of the Department of Agriculture, for development of the catalytic method of producing phthalic anhydride from naphthalene. In 1916 they covered this process by United States Patent No. 1,285,117, assigned to the people of the United States. A complicated patent situation arose later, however, because of the simultaneous discovery of the same process by a German chemist, Alfred Wohl. On account of the war, Wohl was unable to file claims in the United States until several years after his discovery. When application finally was made, following a soft-hearted act of Congress favoring such cases, the I. G. contended that Wohl's invention preceded that of Gibbs and Conover by two months, although there was some question as to whether it had not really followed it by three days. However that may be, the Germans were allowed a United States Patent in 1934, which apparently dominated the Gibbs and Conover claims.

Styrene

Styrene, consumed in huge volumes in the production of GR-S synthetic rubber and, to a less extent, in the manufacture of polystyrene and allied plastics, is also derived from coal tar and light oil.

It occurs to some extent in coal distillates, but its separation in a pure state has not yet been accomplished economically, although impure fractions have, in times past, been produced in very small quantities.

All of the styrene made in the United States today is obtained by pyrolysis of ethylbenzene which, in turn, is derived from benzene by reaction with ethylene or ethyl alcohol, as described in later chapters. Pyrolysis of isopropylbenzene is a potential source of styrene.

Coumarone and Indene

Coumarone-indene polymers represent another important class of resins derived from coal tar and light oil. They are obtained directly from certain naphtha cuts, without separation of the pure monomers, by resinification with sulfuric acid or other suitable catalyst. These resins are not

used for molding purposes, but are employed as binders in mastic floor tile, as components of chewing gum, as bases for printing inks and spar varnishes, and as softeners in rubber compounding.

Coke

The importance of coke to modern chemical industry is equal to that of coal tar, for it serves as a source of water gas, carbon dioxide, acetylene, and calcium cyanamide.

Water Gas. Water gas is formed by passage of steam through red-hot coke. It is a mixture of carbon monoxide and hydrogen, both of which are utilized in the manufacture of chemicals that find their way into many plastics, as illustrated by Figure 5. By high pressure synthesis, hydrogen and carbon monoxide are converted to methanol. This compound was formerly obtained by distillation of hardwood. Today, although wood distillation is still practiced, all but a few per cent of our annual consumption comes from water gas. Formaldehyde, made by oxidation of methanol, is an essential component of all of the large volume thermosetting resins now produced, including phenolics, ureas, and melamines. It is utilized to a less extent in the manufacture of other special purpose resins such as the sulfonamide-formaldehyde resins and polyvinyl formal employed, for example, in magnet wire insulation.

Synthetic methanol also serves in relatively small amount as an intermediate in the most recent industrial method for making acetic acid, a compound used in large volumes by the plastics industry in the production of the semi-synthetic, cellulose acetate. This acetic acid process involves high pressure interaction of carbon monoxide and methanol.

Methanol also enters into the synthesis of other plastics, such as polymethyl acrylate and polymethyl methacrylate.

Carbon Dioxide. In the case of urea resins, coke is the source not only of formaldehyde, but also of carbon dioxide which is converted into the other essential intermediate, urea. Formerly relatively expensive, this compound now sells for about four cents per pound. It is made by condensing ammonia with carbon dioxide under heat and pressure. American production began during the First World War when German imports were shut off. Better than 100 tons were made here in 1920 at a value of about 70 cents per pound. Plastics from urea were then unknown and American manufacture of this chemical, destined only for fertilizer use, ceased in 1922. It began again in 1933 with production of an ammoniacal urea solution and a pure crystalline grade of urea two years later. Meanwhile, the synthesis of urea plastics on an industrial scale had been undertaken in this country in 1929 and expanded rapidly during the 'thirties after introduction of domestic synthetic urea.

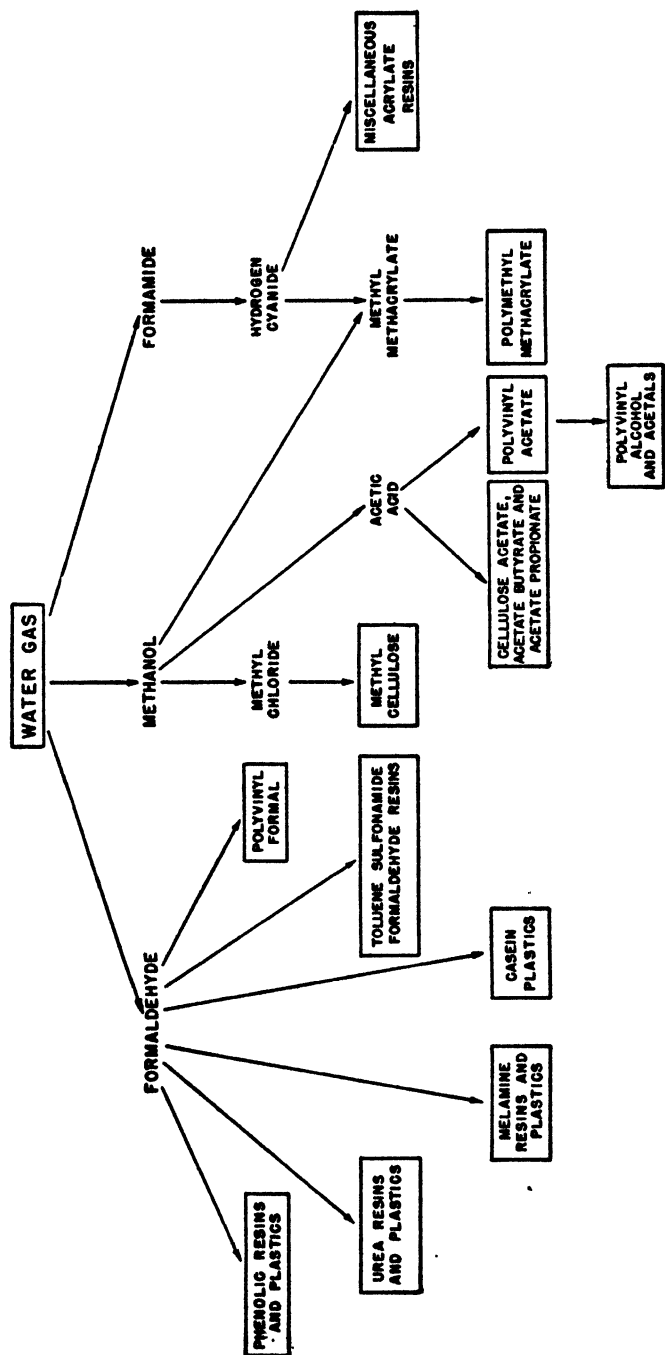


Figure 5. Derivation of synthetic resins and plastics from water gas.

Acetylene. Coke reacts with lime in the electric furnace to yield calcium carbide. This compound is, of course, the common source of acetylene gas, and the latter is now the basis of an extensive chemical industry, which includes the manufacture of certain plastics, as shown in Figure 6. Although formerly used for lighting purposes, acetylene first assumed importance as an industrial chemical during World War I when huge volumes of acetone were required for the purification of nitrocellulose in order to supply Allied needs for Cordite. Addition of water to acetylene, molecule for molecule, yielded acetaldehyde. This chemical was then oxidized to acetic acid and subsequently converted to acetone by means of catalytic pyrolysis involving the use of certain oxides of manganese. Thus, at about the time that electricity began to sound the death knell of acetylene lighting, there arose a chemical industry, founded upon this gas, which has assumed major proportions during the past twenty years and which now supplies a long list of industrial chemicals.

By addition of acetic acid to acetylene, vinyl acetate is obtained and this liquid is converted into a number of vinyl resins whose various chemical and physical properties adapt them to a wide range of uses, from safety glass interlayer to oil-resistant rubber substitutes, artificial silk, and diverse other products.

Through a series of reactions discussed in Chapter 20, acetylene is also converted into "neoprene," an important oil-resistant synthetic rubber.

Among the many derivatives of acetylene, acetic acid and acetic anhydride are outstanding. The methods used for their production have changed several times during the last two decades and several alternative processes have been developed. Both the acid and its anhydride are employed in the synthesis of cellulose acetate, one of the most important of today's semi-synthetic resins. It is fabricated into molded articles, transparent sheet, lacquers, and artificial silk. Two related plastics, cellulose acetate propionate and cellulose acetate butyrate likewise require acetic anhydride for their manufacture.

Acetone, already mentioned, is not only an essential solvent in many operations of the plastics industry, but also enters into the synthesis of a variety of resins. It is, for example, an intermediate in the preparation of the transparent methacrylate resins, the other essential being calcium or sodium cyanide which may be derived from calcium carbide through calcium cyanamide.

During the past few years, German chemical industry has expanded the use of acetylene in organic synthesis. A considerable number of intermediates, besides those just listed, were manufactured on a large scale in Germany by the close of World War II. Many of them had already begun to find their way into synthetic resins and allied products.

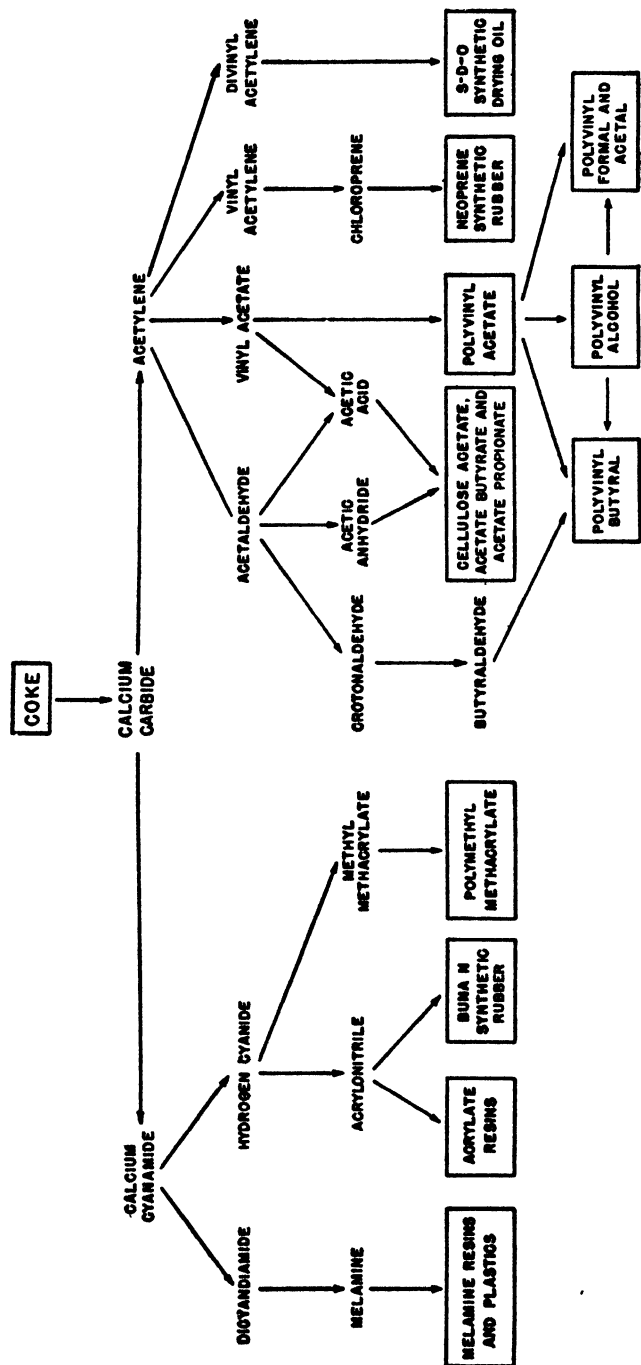


Figure 6. Derivation of synthetic resins and plastics from coke.

Calcium Cyanamide. Calcium cyanamide, manufactured by passing atmospheric nitrogen through calcium carbide in an electric furnace, is an important form of fixed nitrogen. Its principal use is in fertilizers, but it also serves as a source of nitrogen for chemical industry. Calcium cyanide is derived from it and this chemical, in turn, is an intermediate for some of the methacrylate resins. Acrylonitrile, also derived from cyanides, is a necessary intermediate in the synthesis of certain of the less common flexible acrylate resins. More important, it constitutes from 15 to 35 per cent of the oil-resistant synthetic rubbers of the "Buna N" type. Calcium cyanamide also serves as a source of melamine for melamine resins utilized in molded and laminated plastics and in surface coatings. The relation of calcium cyanamide to synthetic resins and plastics is also summarized in Figure 6.

PETROLEUM AND NATURAL GAS

Prior to 1920, coal products served as the principal raw materials for chemical industry. Since then, petroleum and natural gas have been developed as sources of synthetics and are now of equal rank in both volume and diversity of chemical derivatives. It is interesting to contrast the present situation with that which existed some twenty-five years ago. Almost as soon as this nation entered World War I, it was faced with the necessity of producing large quantities of mustard gas, the synthesis of which begins with ethylene. Manufacture of this gas in sufficient amount presented a serious problem which was finally solved by dehydrating alcohol. A plant constructed at Edgewood Arsenal toward the end of the war would have yielded enough ethylene by this method to make 40 tons of mustard gas per day. Today, by contrast, ethylene is available in huge volumes from operations of the petroleum industry and millions of pounds of ethyl alcohol are made synthetically by the reverse procedure of hydrating ethylene—and alcohol is only one of the many chemical products now made from this gas!

Petroleum is constituted largely of a complex mixture of hydrocarbons, ranging all the way from gases like methane, to solids yielding hard asphalts when freed of volatile matter. The number and diversity of hydrocarbons present in petroleum is so great that no one has yet been able to identify more than a small fraction of the different compounds which occur in a given sample from a given source. Their nature depends upon the geological history of the oil, so that there are probably no two fields which give rise to petroleum of exactly the same composition. Chemists at the Bureau of Standards have identified several dozen components of a certain Mid-Continent oil.

Natural gas usually consists chiefly of methane, but it also contains other gaseous and volatile liquid hydrocarbons in smaller amounts. Occasionally gas is found which contains very little methane, being constituted largely of ethane and higher hydrocarbons. Such wells are found particularly in certain parts of the Appalachian area where as high as 70 per cent ethane has been reported.

In order to manufacture chemicals from petroleum or natural gas, it is usually necessary to separate relatively pure hydrocarbons from the complex natural mixtures in which they occur. Partly because of their greater ease of purification, only the lower paraffins—for the most part those which are gaseous at room temperature—have yet found much application in the manufacture of synthetic chemicals.

There are five principal ways by which the hydrocarbon components of petroleum and natural gas are converted to chemicals: (1) pyrolytic cracking followed by chemical reactions of various types, (2) oxidation with steam, carbon dioxide, or atmospheric oxygen, (3) chlorination, (4) nitration, and (5) sulfonation.

Among these various methods for chemical conversion of petroleum hydrocarbons, the last two have not yet achieved much importance in the field of plastics technology.

Oxidation Products

The oxidation of methane can be carried out either directly by means of atmospheric oxygen or by reaction with steam or carbon dioxide. In the last two cases, water gas is produced instead of organic compounds. The production of hydrogen in this way, using natural gas as the source of methane, is worked extensively, particularly for the production of hydrogen for hydrofining. A portion of our present supply of synthetic methanol also comes from such water gas. Here is an interesting example of a field disputed by both coal and petroleum. We shall see other points at which the frontiers of territories occupied by these two raw materials are not clearly delineated.

If atmospheric oxygen (instead of water or carbon dioxide) is used to oxidize methane, a number of organic chemicals are formed. In this case, the engineer is hampered by the difficulty of directing and controlling reaction in such manner that technically pure compounds or usable mixtures are produced. Danger of explosions also constitutes a serious hazard. A few years ago, however, a Mid-Continent oil and gas company began operation of a process in which natural gas is partially oxidized under pressure. The products include alcohols and ketones, offered as solvents. Formaldehyde is one of the principal products and is manufactured in

considerable amounts at a cost which is competitive with that of making it by oxidation of methanol. Formaldehyde produced in this way has been successfully utilized in the manufacture of phenolic resins.

Cracked Gases

Pyrolytic cracking of petroleum and natural gas, followed by separation of more or less pure individual compounds from the cracked hydrocarbons and further conversion of these unsaturates constitutes by far the most important general method of making useful industrial chemicals from oil and gas. The manufacture of carbon black by burning natural gas in the absence of sufficient oxygen to cause complete combustion is well-known. In certain newer, more conservational processes, pyrolysis is carried out by means of heat alone. So-called "soft" or "Thermatomic" blacks of the rubber industry are produced in this way and, in addition, hydrogen is obtained in a degree of purity such that it can be used for high-pressure synthesis of ammonia. Oil refineries can produce hydrogen even more cheaply by catalytic dehydrogenation of naphtha.

In the cracking of petroleum oils, considerable volumes of gaseous hydrocarbons are formed. Depending upon the method of cracking, refinery gases containing up to 40 per cent of unsaturates may be obtained, and these compounds are utilized by chemical industry in the manufacture of a wide variety of intermediates for the production of numerous chemicals, including important plastics and synthetic rubbers. The purposeful pyrolysis of natural gas under controlled conditions has been carried out for more than twenty years for the express object of obtaining ethylene and propylene for conversion into chemicals.

Ethylene. The plastics industry has grown tremendously since the advent of chemicals from cracked gases. Many solvents and plasticizers are derived therefrom; so also are many plastics themselves. The derivation of resinous products from ethylene is summarized in Figure 7. This olefin serves as raw material for the manufacture of vinyl chloride, an important intermediate for the versatile vinyl plastics. Vinyl acetate, another resin intermediate, is made from acetylene at present, but it can also be obtained from ethylene. This interchangeability of source is enjoyed to a greater degree by vinyl chloride, which is actually produced commercially from both ethylene and acetylene. Although the vinyl resins originate with vinyl chloride, vinyl acetate, or a mixture of both, yet the final products include a remarkable variety of types resulting from a diversity of chemical metamorphoses. Finished articles include resin-coated fabrics, transparent sheeting, molded articles, artificial silk, wire and cable insulation, elastomeric materials, and a multitude of other products. American production of all types of vinyl resins was only some-

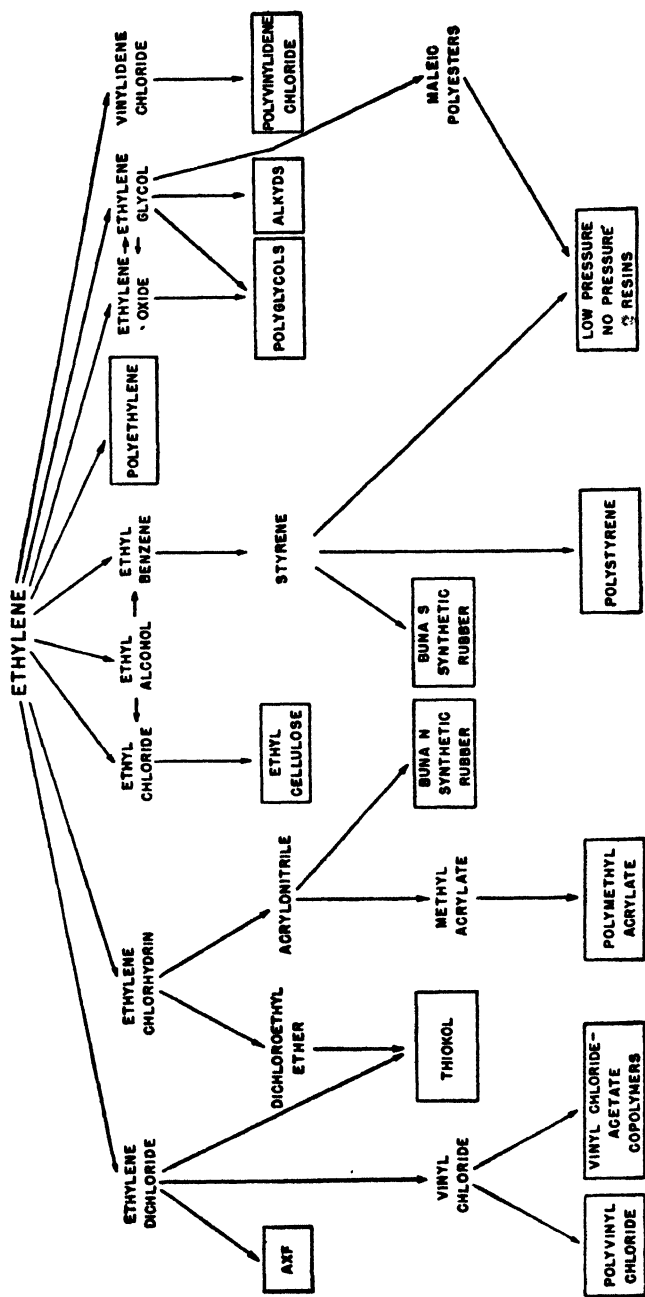


Figure 7. Derivation of synthetic resins and plastics from ethylene.

what in excess of a million pounds in 1935. Today these resins are numbered among the largest volume plastics.

Ethylene from cracked gases is the source of a variety of other plastics such, for example, as polyethylene, essential as an insulating material in radar applications. Polystyrene, previously noted, is derived in part from ethylene. This gas is also an intermediate for the manufacture of ethyl cellulose, used in molding powders, lacquers and transparent sheets and foil. In this case, ethylene is first converted to ethyl chloride, a compound which finds other important uses as a refrigerant and in the manufacture of many non-resinous commercial chemicals, among which lead tetraethyl is consumed in greatest quantity.

Ethylene can also be converted into vinylidene chloride. This compound is readily polymerized to a resinous material, polyvinylidene chloride, which was first placed on the market under the trade name "Saran" in 1939. Tubing, pipe, film, filaments, and molded articles of this material are now important commercial articles.

Ethylene dichloride, another chlorinated derivative of ethylene, is one of the intermediates for "AXF," a more or less rubber-like substance made by reaction with aromatic hydrocarbons. It is used in compounding natural rubber to improve oil resistance. Another elastomer is produced from ethylene by reacting either the dichloride, or related compounds, with sodium polysulfide. Such substances are extremely oil-resistant.

Ethylene is also one of the source materials for acrylonitrile, an intermediate in the production of some of the soft acrylate resins and an essential component of synthetic rubbers of the "Buna N" type.

Propylene. Not only ethylene, but propylene and the butylenes have also become important raw materials for the production of plastics as summarized in Figure 8. A goodly portion of the cellulose acetate manufactured in this country can be traced to petroleum through propylene. This situation warrants closer scrutiny. Among industrial chemicals derived from propylene, isopropyl alcohol is the oldest, having been manufactured in this way for nearly twenty years. The volume of this alcohol increased from 37,500 gallons in 1922 to 50,000,000 gallons in 1944. This remarkable increase in production resulted from expanding applications made possible by price reduction from \$2.00 to 31 cents per gallon during the same period. Acetone is now made from isopropyl alcohol by oxidation at a cost which is not only competitive with that of older methods, such as corn starch fermentation, but which has lowered the price of this widely used solvent to such a point that it can be employed as an intermediate for the production of cheap acetic anhydride, a chemical now selling at a figure equal to about one-third its 1930 quotation. Because of the resultant lowered price of this anhydride, the production of cellu-

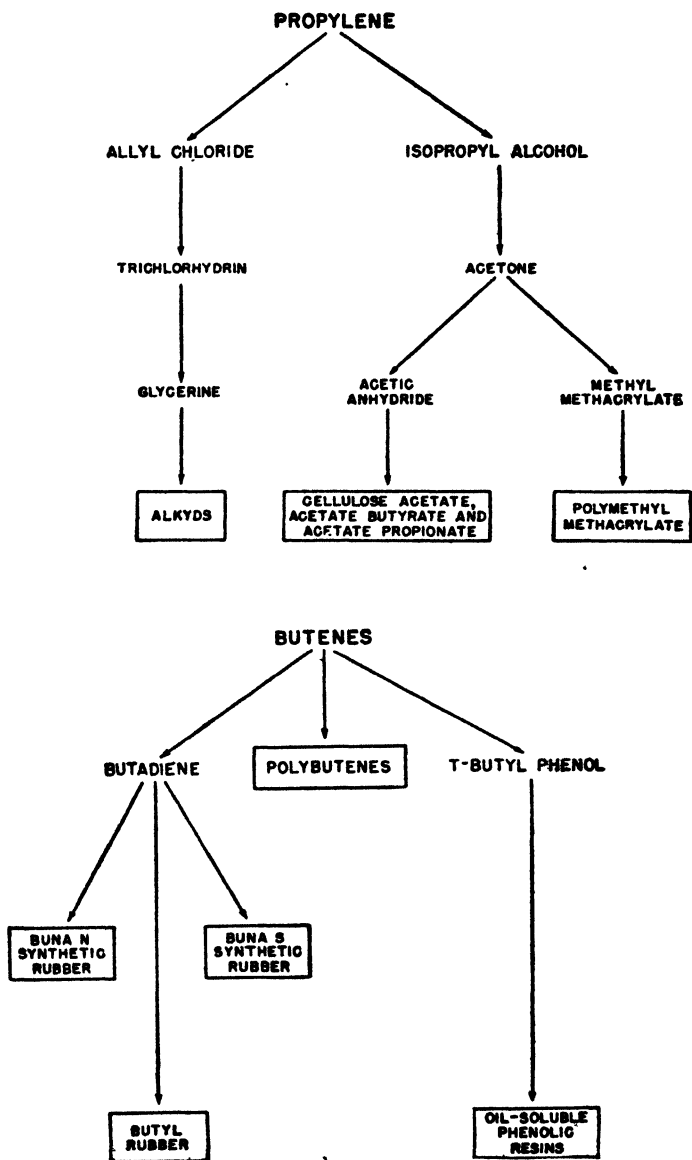


Figure 8. Derivation of synthetic resins and plastics from propylene and the butenes.

lose acetate has increased progressively until it has now passed the 200 million pound mark. Cellulose acetate is used in moldings ranging from transparent oil cans to automobile steering wheels, light shades, and boudoir mirror frames. In sheet and film form it has opened large markets in the packaging and photographic fields and as filament it has become well established in artificial silk, a use which is expanding annually.

The sphere of influence of cheap acetone from propylene in the world of plastics is not limited to cellulose acetate. It is also an intermediate in the manufacture of the transparent methacrylates, "Lucite" and "Plexiglas." The exceptional clarity of these resins, exceeding that of glass, has resulted in essential applications in the fabrication of transparent airplane enclosures, lenses, light bending and reflecting devices such as surgical instruments and edge-lighted signs, novel furniture, and innumerable other articles.

The production picture of acetone, acetic acid, and acetic anhydride is very complex, because of the fact that the same chemicals are economically produced from several raw materials by competing methods, and even by several different chemical processes starting with the same raw material. It is therefore difficult to ascertain exactly how much of some of these large tonnage chemicals is actually derived from petroleum instead of coke or some other source. Acetone, for example, is made (1) by the destructive distillation of calcium acetate obtained as a by-product from wood alcohol manufactured by hardwood distillation, (2) from acetic acid obtained by direct extraction of pyroligneous acid from wood distillation, (3) from acetic acid derived from acetylene, water, and oxygen, (4) by fermentation of corn starch, in which operation it is produced simultaneously with *n*-butanol, and (5) by oxidation of isopropyl alcohol made from propylene gas. Although much of the acetone now made in the United States comes from propylene, all of the other methods just mentioned are producing or have done so in the immediate past. The Fernbach-Weizmann fermentation of corn starch—initially developed in France in order to supply raw materials for synthetic rubber—operated by the Commercial Solvents Corporation and developed during World War I, was responsible for much of the domestic acetone until manufacture from petroleum began.

Chemicals from cracked gases have invaded the important field of alkyd resins, utilized in large volume for paint and varnish applications. While the dibasic acids from which they are made now come chiefly from coal tar by oxidation of either naphthalene or benzene, the Carbide and Carbon Chemicals Corporation now manufactures maleic acid, used increasingly for alkyd resin production. Although the latter company's method of manufacture of this chemical has not been announced, the

general structure of their business leads one to infer that it comes from cracked petroleum gases. Glycerol, or occasionally some other related compound, is the other essential component of alkyd resins. At the present time, domestic glycerol comes entirely as a by-product from the soap and fat-splitting industries. During World War I, a fermentation method was developed in Germany to augment dwindling fat supplies, but similar processes never gained an important foothold in this country. The selling price of glycerol has fluctuated erratically between 10 cents and 32 cents per pound during the last twenty-five years. This condition, coupled with the fact that consumer demand appeared relatively stable and fixed at volumes which could be easily supplied by the soap industry, has tended to discourage the development of synthetic processes for its manufacture. In 1940, however, operation of a pilot plant for making glycerol from propylene was announced by Shell interests. It appears probable that increasing demands for this chemical in alkyd resin production, cellophane plasticization, and other applications—as well as explosives—will result in future commercial evolution of this developmental operation.

Higher Hydrocarbons. From the butenes have come a number of new elastomers, or rubber-like materials, including the polybutenes and "Butyl" rubber. Butadiene is obtained in tremendous volumes by various cracking operations applied to petroleum products. These processes are discussed in Chapter 20. Butadiene is the fundamental building block in the synthesis of GR-S and the "Buna N" type elastomers. Rapid development of domestic production to its present prodigious scale was indeed among the chemical wonders of World War II.

Both C_4 and C_6 paraffins and olefins are also utilized in the production of special phenols, employed in the synthesis of oil-soluble phenolic resins destined for paint and varnish purposes. Development of natural petroleum phenols for plastics manufacture is currently underway.

The higher olefins have not been used as extensively in chemical synthesis as those containing four carbon atoms or less. Their limited applications in the field of plastics include varnish bases, such as polymer slop, "Santo Resin" made from special highly cracked petroleum fractions, and synthetic drying oils which are produced by polymerization of highly cracked distillates and which serve as substitutes for linseed and tung oils.

FIXED NITROGEN

The nitrogen content of the earth's atmosphere is also a raw material of prime importance for many plastics. Gaseous nitrogen from this seemingly inexhaustible source is fixed either by high pressure hydrogenation to ammonia or by conversion to calcium cyanamide as a result of passage through hot calcium carbide. Other less economical methods are known,

but are not operated in the United States. For many years the only commercial sources of nitrogen were Chilean nitrate and ammonium sulfate obtained as a by-product from coal carbonization.

Because gaseous nitrogen reacts difficultly with other substances, its fixation did not become a factor until shortly before World War I. Hydrogenation of atmospheric nitrogen to ammonia required the perfection of an entirely new engineering technique of high pressure synthesis. This technique has since been applied to the manufacture of many other industrial chemicals, including synthetic methanol, higher alcohols used in detergents and wetting agents, and hydrofined petroleum oils.

Fixed nitrogen, either as ammonia or calcium cyanamide previously discussed, is essential for the production of the ureas, melamines, polyamides, acrylates, methacrylates, butadiene rubbers of the "Buna N" variety, and several other resins of smaller sales volume, such as the sulfonamides.

MISCELLANEOUS RAW MATERIALS FOR SYNTHETIC RESINS

Other substances also serve as raw materials for various synthetic resins. Modifying agents for phenolics and alkyds, used in surface coating formulation, include drying and semi-drying oils, and fossil and recent resins such as copal and rosin. Turpentine is also used in the manufacture of a limited number of resins employed in lacquers, adhesives, and paper coatings.

RAW MATERIALS FOR SEMI-SYNTHETICS

Let us glance now at the sources of raw materials for the semi-synthetics. Included among them are a number of very different products of natural origin: rubber, cellulose, lignin, casein, and other proteins.

Rubber

Natural rubber serves not only as the source of its familiar vulcanized products, both soft and hard, but also as the basis of a group of resins which have found use during the last fifteen years in compounding acid- and alkali-resistant paints, lacquers, and adhesives, and in the manufacture of transparent sheet and foil resembling cellophane in appearance.

The chemical nature of rubber is altered by isomerizing it with many agents which do not, themselves, enter into the structure of the final product. These modified forms of rubber contain the same proportion of carbon and hydrogen as rubber itself, but the component atoms are arranged in a slightly different manner with respect to each other. Products of this nature are made commercially from rubber by treating it with sulfuric acid, stannic chloride, or the like. Their principal uses are

as resinous bases for acid- and alkali-resistant paints and for adhesives employed especially in bonding rubber to smooth surfaces, for example metals.

An older product is chlorinated rubber, made by the action of gaseous chlorine on unvulcanized rubber. This semi-synthetic has found use in the formulation of acid- and alkali-resistant surface coatings, especially in physical admixture with alkyd resins.

Hydrogen chloride can also react directly with unvulcanized rubber, and the product, known as rubber hydrochloride, is cast into transparent films for decorative and wrapping purposes. In another form, it is used as a special adhesive. The shortage of natural rubber has led to the development of analogous chemical derivatives of various synthetic polymers of diolefins, especially isoprene.

Cellulose

By far the most important semi-synthetics are made from cellulose. Nature has been particularly lavish in her distribution of this raw material which is formed by all vegetable matter and which consists of large, complex molecules built up, supposedly, from carbon dioxide and water. Cellulose varies somewhat in its physical and chemical characteristics, depending upon its source. It is universally present in the cell walls of all plants. When these walls are thick, strong fibers result which are used industrially in enormous quantities for the manufacture of paper, textiles, twine, and cord. Smaller amounts are used in the production of vulcanized fiber. These vital industries take nature's all-important plastic, cellulose, and fabricate it into forms useful to man without substantial chemical alteration.

Semi-synthetic plastics are derived from cellulose by changing its chemical nature. They are of three principal types:

(1) Regenerated cellulose, fabricated by conversion of natural cellulose into a soluble derivative and then re-precipitation in different physical form from that in which it occurs in nature. It is represented chiefly by viscose rayon and transparent film such as cellophane.

(2) Cellulose esters, made by causing cellulose to react with either organic or mineral acids. This family includes cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, and cellulose nitrate. Applications are legion, varying from artificial silk to packaging and photographic film, lacquers, explosives, and molded objects.

(3) Cellulose ethers, produced by the action of alkyl halides on alkali cellulose. Methyl cellulose and ethyl cellulose are the most important commercial representatives of this class. Carboxymethyl and hydroxyethyl cellulose, as well as benzyl cellulose are manufactured in smaller volumes.

Methyl cellulose is used as an emulsifying agent, textile treating agent, and size for paper. Ethyl cellulose finds application in transparent film, electrical insulation, and molded and extruded plastics.

Wood Pulp. The most important sources of cellulose are wood and cotton. These two products are the principal raw materials of the paper and cotton textile industries, respectively. In addition to them, flax, hemp, manila, and sisal are used in certain textile and cordage products. Cereal straws and esparto are also employed by the paper industry. Sugar cane bagasse is the principal raw material in the manufacture of insulating and building board like "Celotex."

Wood pulp for the paper industry is manufactured either by purely mechanical means or by chemical treatment. Approximately thirty per cent of North American production, largely Canadian, is made by mechanically tearing apart the fibers of barked and washed bolts of cut timber. Spruce is most often employed in this process which is carried out by forcing the bolts lengthwise against a rapidly rotating abrasive surface in the presence of water. Depending upon the amount of water used, the process is either hot or cold. Longer and coarser fibers are obtained by the cold method. Pulp produced mechanically is suitable only for the manufacture of cheap paper such as newsprint. It is really only finely divided wood retaining all of its original lignin and resin content.

For the manufacture of both the better grades of paper and the semi-synthetic plastics derived from wood pulp, the latter must be treated by chemical methods in order to free it from non-cellulosic constituents. Cellulose, itself, makes up only about 50 per cent of the wood substance. Lignin and resins are present in greater or less amounts, depending upon the botanical origin of the wood. There are three methods of chemically processing wood pulp to eliminate its lignin and resinous components. They are known as the sulfite, soda, and sulfate (or kraft) processes. In all of them, the wood is first chipped and sieved.

In the sulfite process the chips are cooked with steam in a solution of calcium bisulfite, then washed, screened, lapped, and dried. About fifty per cent of the domestic wood pulp production is made in this way primarily from spruce, hemlock, and balsam.

The soda process involves digestion of the chips under pressure in a solution of sodium hydroxide at 240° F. This method is applicable to such hardwoods as aspen, but is also used for pines, in particular southern pine.

The sulfate process is applicable to coniferous woods possessing a high resin content, such as southern pine and lumber mill wastes. Hemlock, spruce, tamarack, jack pine, and balsam fir are also reduced by this process in less amounts. Chips are digested with a solution of caustic,

sodium sulfide, and sodium sulfate. After cooking, the pulp is washed, screened, and dried as usual. This process is used for the manufacture of kraft paper, but the increased production of relatively cheap chlorine has made possible inexpensive bleaching operations so that sometimes even as many as four bleaches may be applied. As a result, a high-grade pulp is obtained which is competitive in price with that obtained by the sulfite process.

The alpha cellulose content of chemical pulp runs from 90 to 96 per cent, even higher occasionally. Pure cellulose is a necessary prerequisite for the manufacture of all semi-synthetic cellulosic plastics. Although cotton linters are often preferred for the manufacture of esters and ethers of cellulose, chemical pulp is sufficiently pure to serve as raw material for regenerated cellulose. It supplies approximately 80 per cent of the cellulose converted into rayon and transparent cellulose packaging material like cellophane. For rayon manufacture, cotton linter cellulose is sometimes blended with it to the extent of 25 per cent. Chemical pulp is also used to some extent in the manufacture of cellulose nitrate.

Cotton. Cotton is the purest naturally occurring form of cellulose, containing about 90 per cent thereof. The cotton plant has been cultivated in sub-tropical climates for centuries. Between 1500 B.C. and 1500 A.D. India was the center of the industry, but today the United States, Egypt, and Brazil are the chief exporting countries. From 40 to 50 per cent of the world's supply is grown on about 37,000,000 acres of land within the Cotton Belt of this country.

Although a perennial, cotton is grown as an annual crop, the plants being cultivated in rows varying from two and a half to six feet apart, with a few inches between plants in each row, or with several plants grouped together in hills twelve to fourteen inches apart. Red and white flowers first appear, then mature into four- or five-valved cotton bolls that contain from 32 to 36 seeds apiece to which some 8000 cotton hairs are attached. The natural function of these hairs is probably to permit the wind to scatter the seed after the boll has ripened and burst, much as the achenes of the dandelion are disseminated by the tufts of hair attached to them. The staple fibers of cotton vary from $\frac{3}{8}$ inch to over 2 inches in length, depending upon the species. Practically all staple fiber is utilized in the manufacture of textiles.

After the cotton is removed from the seed by ginning, there remains a fuzzy covering of down, called linters, which formerly was discarded. When the United States entered World War I, the increased demand for cellulose led to issuance of an order by the War Industries Board requiring the principal cottonseed oil mills to install additional delinting machinery. After the war, chemical utilization of cotton linters became

an important problem. Today they are a prime source of cellulose for the manufacture of nitrate, acetate, and ethyl cellulose.

Ginned cottonseed are cleaned and then delinted by passage through a machine in which they come in contact with saws revolving at high speed. The non-cellulosic impurities are removed by several hours' cooking with about 3 per cent caustic soda under 40 to 80 pounds of steam. The digested linters are then washed free of caustic, bleached with chlorinated lime, sometimes treated with an anti-chlor, and then thoroughly washed and dried. The purified product, known as *alpha cellulose* (a term applied to grades of cellulose which are insoluble in caustic solution), represents about 75 to 80 per cent of the original weight of linters and averages 99 per cent purity.

Lignin. In the manufacture of wood pulp, large volumes of waste liquors are produced. Those from the soda and sulfate mills are evaporated and the residue burned. By suitable treatment of the ash, from 85 to 90 per cent of the original chemicals are available for re-use. Recovery is a necessary feature of the economics of these processes. In the case of sulfite operations, however, waste liquor is discharged into nearby streams, resulting in obnoxious pollution. We have already seen that 25 to 30 per cent of the wood substance is lignin. This is all contained in the waste sulfite liquors. It would be possible to recover one and a half million tons of lignin from the waste liquors of pulp mills every year, were an effort made to do so. Added to this are several million tons of lignin which could be supplied annually from forest and sawmill wastes, while enormous amounts are potentially available from such annual crops as sugar cane bagasse, cornstalks and cereal straws. Nearly three and a half million tons of bagasse, for example, are produced annually in the United States, Puerto Rico, Hawaii, and the Philippines, while only 150,000 tons are converted into insulating and building boards.

Current developments are under way to utilize at least a portion of the lignin content of all these industrial wastes. Several products made from waste liquors and varying from tanning agents and adhesives to additives for Portland cement and synthetic vanillin are on the market. Both laminating and molding resins have been developed from lignin.

In addition to plastics derived from lignin recovered from waste liquors, another semi-synthetic plastic has been produced in times past by exploding and compressing wood chips. In this product, which has now been removed from the market, the activated lignin content of the chips served as binder.

Proteins. Several plastics are derived from proteinaceous raw materials. Among proteins so used, casein is the oldest. It occurs to the extent of three or four per cent in normal whole milk. After separating the cream

by centrifuging, the casein is precipitated with either dilute acid or rennet at a slightly elevated temperature. It is then washed and dried. Its principal use is in paper coating but appreciable amounts are also employed in plastics, casein wool, adhesives, paints, insecticidal sprays and miscellaneous applications. The product utilized by the plastics industry is precipitated exclusively with rennet. Acid-precipitated casein is used in the production of synthetic fibers.

Natural proteins from other sources are currently being explored as raw materials for semi-synthetic plastics and related products such as fibers. Soybean protein and corn zein are the most important.

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Chapter 4

General Chemical Principles of Resinification

The organic chemist is essentially an architectural engineer. His structures are of molecular dimensions, but despite their invisibly minute nature he is vitally concerned with their size and geometrical aspects and with the constructional materials used therein. The plastics technologist is no less interested in the architecture of his materials than the orthodox organic chemist who deals with smaller and more conventional molecules. Time was when a special set of rules was thought to apply to resinous materials. Numerous hypotheses have been proposed and discarded concerning the possibility that these substances might be composed of large agglomerations of many small molecules united in physical association. It is now universally accepted, however, that they are built up of large molecules whose fundamental structures comprise chemical bonds no different from those which exist in the simplest organic compound, methane.

The significant distinction between conventional low molecular weight organic compounds like ethyl alcohol or benzene and resinous materials like polyvinyl chloride or the phenoplasts is primarily one of size of the component molecules. Resinous materials may vary in molecular weight from only a few hundred to several hundred thousand—possibly a million or two in some instances. Many of the physical and, to some extent, even the chemical properties of synthetic and semi-synthetic resins are directly related to their molecular weight.

Geometrical Aspects

In a large molecule, structural relationships play a very important role. Where its skeleton is constituted of a long linear chain of atoms, its thread-like character, despite its randomly kinked nature, confers upon it quite different properties from those associated with a molecule built around a closely inter-locked, three-dimensional skeleton.

Thermoplastics. The former type of resin is thermoplastic, that is, it can be softened and sometimes melted by application of heat without undergoing appreciable chemical change—provided it is not carried above its decomposition point. Upon cooling, it resumes its original solid condi-

tion. This operation can be repeated as often as desired. Polystyrene and most of the vinyl resins are typical thermoplastics.

It is unnecessary for the linear chain of a thermoplastic to be composed solely of carbon atoms as in the families just cited. It may contain other elements as well, as in nylon. It may also consist of a linear association of rings, like loops in a chain, as in cellulose derivatives.

Thermohardened Resins. Where the structural skeleton of a resin consists of an interlocked network of bonds, the substance is much less sensitive to heat and will not melt or soften appreciably below its decomposition point, although a limited amount of shaping may be practicable by careful application of heat and pressure. Plastics of this type are designated thermohardened inasmuch as they remain hard and unmoldable upon heating. We shall see in subsequent chapters that thermohardened plastics may be produced in some cases by carrying out resinification of suitable intermediates at room temperature or slightly above it. In other instances, application of considerable heat during molding is essential. In the latter case, the substance is already partially resinified and use of heat, ordinarily with pressure, completes its conversion to a still higher molecular weight, more cross-linked structure. It is then designated as a thermosetting plastic for it is set (or cured) by heat. Uncured thermosetting resins can be softened a limited number of times or for a limited period by heating. If the time and temperature are sufficiently prolonged, however, chemical reaction sets in, complex tridimensionality is developed, and the resin hardens while still hot. It remains hard, regardless of whether it is further heated or cooled and reheated. Straight phenolic and urea resins are typical thermosetting plastics.

Tridimensionality may also sometimes be developed by causing a thermoplastic to react with an extraneous chemical which is capable of cross-linking the long linear resin chains. Reaction of this kind is, of course, predicated upon the presence of specific active groups in the resinous molecule and may be carried out either at room temperature or above. A case in point is the vulcanization of rubber with sulfur. Thermohardened resins produced in this manner are occasionally called chemoset or chemosetting plastics.

Relation of Structure to Properties. Thermoplastic and thermohardened resins constitute the two major divisions of the plastics field. As a rule they are differentiated from each other in (1) methods of synthesis, (2) means of fabrication into molded shapes, (3) chemical structure (linear versus tridimensional), and (4) physical properties. Because of the complexity and rigidity of the molecule, resins whose skeletons are cross-linked, or tridimensional, are far less soluble and are harder than products of the same molecular weight which are linear. As noted above,

they are much less susceptible to heat. They are far less extensible, stiffer, and possess greater resistance to deformation under both heat and load than linear structures. Tridimensional resins exhibit much less cold flow than linear ones.

As the chemistry and technology of plastics develop, however, more and more borderline cases appear. Many families of plastics, such as the phenolics, alkyds, and allyl resins, for example, include both thermoplastic and thermosetting members. Hence, an absolutely clean-cut line of demarcation between these two groups becomes more and more difficult. It is desirable to have some way of relating tridimensional to linear molecules. Although not entirely accurate in every case, let us suppose that tridimensional molecules are built up by establishment of bridges of some sort, either direct valencies or radicals, between several linear chains, according to Figure 9.

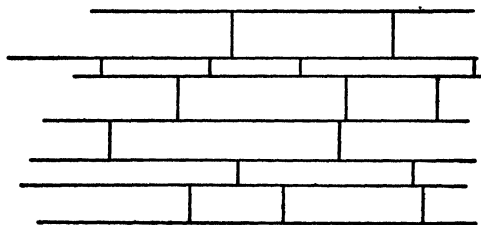


Figure 9. Schematic representation of cross-linked chains.

The more of these bridges, or cross-linkages, which exist per unit length of chain, the more complex the tridimensional character of the molecule and, in a group of otherwise similar products, the greater the abrasion- and heat-resistance, and the less the solubility in both organic solvents and water. Density is increased. Cold flow is decreased. Reversible extensibility is also diminished. The complexity of this cross-linked network may be given a semi-quantitative characterization in terms of its netting index which is the number of bridges per hundred chain linkages. A netting index of 7, for example, indicates that, on the average, the resin under consideration possesses seven bridges per hundred linear bonds. Unfortunately, present knowledge permits only guess-work in the assignment of netting indices to various plastics; but the following table, proposed by Mark, at least serves the useful purpose of suggesting the relative approximate complexity of the molecules of certain commercial plastics.

The netting index of a resin is of practical significance not only with respect to methods of molding and preparation of solutions for surface coating, for example, but also as regards its ability to form films and, especially, filaments.

Table 1. Hypothetical Netting Indices of Certain Polymers¹⁵

Substance	Netting Index
Native cellulose	Nearly 0
Native rubber	Nearly 0
Polybutene	Very low: 3-5
Polystyrene	Very low: 3-5
Polyvinylchloride	Very low: 3-5
Polybutadiene (unvulcanized)	Medium: 5-10
Soft vulcanized rubber	Medium: 5-10
Hard rubber	High: 10-20
Buna N or S (unvulcanized)	High: 10-20
Phenolics (thermoset)	Very high: about 50

Crystallinity in High Polymers. The relation of structure to filament formation has been admirably indicated by Carothers⁴ in the following words: "The qualities necessary for a useful fiber appear to be associated with a very high molecular weight linear polymeric structure and a *certain degree of crystallinity* or definite order in the arrangement of the molecules. The relation between molecular structure and arrangement and the physical properties of fibers has been most clearly recognized and discussed by Meyer and Mark. In a natural cellulose or silk fiber the long molecular chains are arranged in an ordered fashion parallel with the fiber axis. This state of affairs is symbolized as follows:

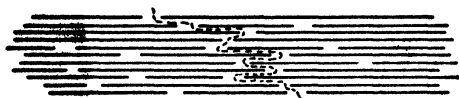


Figure a

This arrangement provides the maximum possible strength in the direction of the fiber axis since the mutual cohesive force of the long chains is fully utilized. To rupture the fiber it is necessary to cause the chains to slip past one another against this cohesive force as indicated in the dotted

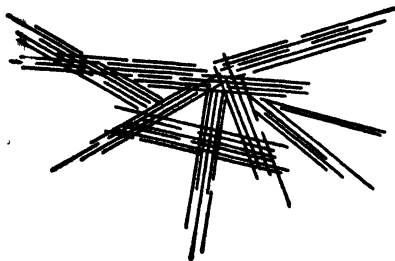


Figure b

line. A transparent sheet of regenerated cellulose shows (by x-ray patterns) a certain degree of order in the arrangement of its molecules, but there is no general orientation. This state of affairs is symbolized in Figure b. *This more or less random arrangement of ordered molecular aggregates can be brought into the more highly ordered state symbolized*

in Figure a merely by the action of mechanical stress. Thus the strength of a sheet of Cellophane that initially has approximately the same strength in all directions can be so changed, merely by careful stretching, that its strength along the axis of stretch is increased several fold. At the same time its strength along the axis normal to its stretch is considerably diminished. The strength of a rayon filament can be increased several fold by the action of stress while it is in the spinning bath, and a comparison of the x-ray patterns shows a much higher degree of orientation along the fiber axis in the filament formed under stress. For a rough mechanical analogy of the mechanism of this process one may picture a disordered mass of long straws (molecules) coated with a semi-fluid adhesive (cohesive force). The gradual application of stress to such a mass would finally bring the straws into parallel alignment where they would more strongly cohere and resist the further action of stress.

"The peculiarities of high polymers are nowhere more strikingly exemplified than in this curious ability to accept permanent orientations through the action of mechanical stress. The properties of simple organic compounds are, generally speaking, independent of their physical history; they are completely determined by the nature of the molecules. Very large molecules, however, are not capable of adjusting themselves instantly to any changes in physical environment, and the properties of a very high molecular weight material may vary over a wide range depending upon the physical treatment it has received."

This knowledge has been applied industrially in the manufacture of nylon, during the spinning of which mechanical stress is applied in order to increase fiber strength. The same operation is also carried out in the manufacture of filaments from polyvinylidene chloride and polyethylene, as well as in high strength hydrolyzed cellulose acetate and other fibers. Molecular orientation is well-known to nature in her synthesis of tendon.

It was once supposed that the essential characteristic of all resins was lack of crystallinity. It is now known that where the molecular structure is quite symmetrical, there is a very definite tendency for high molecular weight substances to assume a microcrystalline structure. It seems probable that in many cases—such as rubber and cellulose, for example—crystallinity in high polymers differs from that in conventional low molecular weight compounds in that a single linear molecule is not necessarily confined within the limits of a single crystalline region, but may traverse several of these areas while passing through intermediate disordered states.

Molecular Size

We have seen that many of the physical and chemical properties of resinous materials are contingent upon the geometrical structure of their

molecules. It is no less true that a large number of the physical and chemical properties of these materials, as well as their commercial applications, are determined in large measure by their molecular weight. This situation is particularly true in the case of linear thermoplastics where this property can be more readily regulated and more easily estimated than in thermohardened materials.

Classification. Inasmuch as the molecular weight of resinous compounds may vary from only a few hundred to several hundred thousand, it is desirable to subdivide the field according to order of magnitude. Staudinger has proposed the following classification:

Hemicolloids. Resinous substances having a molecular weight up to about 10,000. Their degree of polymerization usually runs from 20 to 100. These materials are either brittle solids which can readily be reduced to a fine powder, or glue-like masses. They dissolve without swelling and their solutions are low in viscosity, a factor of prime importance in their principal commercial applications—the formulation of surface coatings and adhesives.

Mesocolloids. Resinous substances having a degree of polymerization ranging from 100 to 1000. These substances are much tougher and therefore much less friable than the hemicolloids. They usually swell to some extent before dissolving. Their solutions are relatively viscous. They are frequently used commercially in the fabrication of molded objects. Films and filaments can often be produced from mesocolloids.

Eucolloids. Resinous substances having a degree of polymerization exceeding 1000. These materials are very tough. Strong films and filaments can readily be produced from them. They often show marked reversible extensibility and are technically useful because of their rubber-like properties. They swell enormously before dissolving and yield highly viscous dilute solutions.

Relation of Size to Properties. In general the effect of increasing molecular weight in a linear resin is to increase heat resistance, hardness, tensile strength, impact strength, abrasion resistance, and reversible extensibility. Film- and filament-forming capabilities are increased. Solubility is decreased with attendant development of swelling phenomena and high viscosity in dilute solutions.

Molecular Weight Determination. Numerous experimental methods have been proposed for the determination of the molecular weight of resinous substances. For estimation of the molecular weight of conventional organic compounds, cryoscopic and ebullioscopic methods are well-known to every chemist. They can be applied to resinous materials whose molecular weight is not in excess of about 10,000. Above this limit, however, it is necessary to resort to some other means of measurement. Indeed, until recent years there have been no other satisfactory ways to

determine very high molecular weights and this fact has perhaps been the greatest single deterrent to elucidation of the nature of many high polymers. Even today there is much uncertainty about this matter and none of the methods now used is beyond suspicion. It is at present believed that the most reliable results are obtained either by osmotic pressure measurements or by means of ultracentrifugal sedimentation, although the former are inaccurate above about 100,000.

A purely chemical way of determining the molecular weight of resinous materials depends upon the presence of a known number of some particular radical in the molecule. This is called the "end group" method because usually the radical in question is located at either one or both ends of the principal chain. Such end group determinations can be applied to only a very limited number of resins in which the presence of a reactive group at the end of the chain can be established with certainty. A case in point is the high polymer obtained by self-condensation of ω -hydroxydecanoic acid.

The first reasonably satisfactory method for approximate estimation of high molecular weights was developed by Staudinger and is based upon viscosity measurements. Although values obtained in this way are subject to many inaccuracies and although the method has been caustically criticized, it remains the most widely used procedure and the one which is of greatest technical merit, for viscosity measurements give information which is not only valuable from a theoretical point of view, but which is also of great significance from the practical angle in the formulation of surface coatings, adhesives, and allied products. Viscosity determinations are of inestimable value in plant control operations and offer a useful means of grading various commercial resins. Staudinger established the empirical fact that in dilute solution, the specific viscosity of high polymers is directly proportional to the length of chain of such compounds and hence to their molecular weight. His relationship states that

$$M = \frac{\eta_{sp}}{K_M \times C}$$

where M is the molecular weight of the compound, C is the basic molarity of the solution, i.e., the molar concentration in terms of the monomeric unit present, and K_m is a constant which varies for different polymeric series and has to be determined by cryoscopic or other methods before it can be applied to viscosimetric calculations. The specific viscosity of the solution, η_{sp} , is equal to $\eta_r - 1$, where η_r , the relative viscosity, is the ratio of the viscosities of solution to pure solvent at the same temperature.

Upon the basis of this relationship, established experimentally in the case of the lower members of various series and extrapolated, as a good

guess, to far more heavy ones, Staudinger and his students determined the molecular weights of a variety of linear polymers. Because of the empirical nature of this relationship and the audacity of extrapolation to magnitudes far in excess of those at which it was verified experimentally, the viscosimetric method of determining molecular weights has received much criticism and has never been accepted with too much confidence, despite its utility and general use. In 1939, M. L. Huggins of the Eastman Kodak Research Laboratories, on purely theoretical grounds, derived a relationship between the specific viscosity of solutions of linear molecules and their molecular weight. He arrived at a direct proportionality having the same form as Staudinger's empirical equation, but in which certain other symbols having a more tangible physical reality replace those of Staudinger.

It is important to note that the viscosity method measures the chain length of a high molecular weight compound, not the actual molecular weight. If the chain is constituted of a series of equivalent units, as in the case of cellulose derivatives or rubber, the law holds, but if the compound is too complex in structure for the molecular weight to be calculated as a simple function of chain length, the viscosimetric method is useless and some other procedure must be adopted.

The definition of molecular weight of high polymers by viscosimetric methods leaves much to be desired despite its more or less theoretical validity. Not only are consistent results difficult to obtain, but the applicability of Staudinger's relationship is so hazardous that apparent molecular weights so measured may be in error by 500 per cent or more. The values commonly reported for vinyl polymers are an example of this state of affairs—most of them are far too low. Industrial practice, therefore, has been directed toward defining the molecular size of macromolecular substances in terms of the viscosity of their solutions under certain standard conditions, rather than as molecular weight. In the case of cellulose nitrate, for example, molecular magnitude is indicated in terms of seconds, referred to in the Hercules' falling ball method described in Chapter 22. In the case of polyvinyl acetate, Shawinigan's lead has been followed by listing these resins in terms of the absolute viscosity at 20° of benzene solutions which contain the equivalent of one mole of monomer per liter. (If measurement is made with an Ostwald viscosimeter, absolute viscosity of the solution can be calculated from the expression:

$$\eta_s = \frac{\eta_B \times d_s \times t_s}{d_B \times t_B}$$

where η_s is the absolute viscosity of the solution and η_B is the absolute viscosity of benzene—both at 20°, t_s is the time of efflux of the solution in

seconds at 20°, d_s is the density of the solution and d_B and t_B are the corresponding values for benzene.)

Polymers and copolymers of vinyl chloride, on the other hand, are defined in terms of the specific viscosity of dilute solutions of specified concentration in appropriate solvents, such as nitrobenzene or methyl ethyl ketone. The specific viscosity, as above noted, is equivalent to $\eta_r - 1$, where η_r is the relative viscosity, $\frac{\eta_s}{\eta_{MEK}}$, for example.

It should be noted that the viscosity of concentrated solutions of high polymers, such as those containing 10 to 15 per cent solids, by no means parallels their absolute viscosity in dilute solutions at about 1 per cent concentration or less. While the latter may be used for calculation of molecular weight according to the Staudinger method, the viscosity of solutions of high solids content depends upon numerous other factors besides chain length, evaluation of whose importance is usually not feasible. The past history of the resin is often of great significance. In the case of cellulose acetate, for example, materials prepared from wood pulp and from cotton having the same viscosity in concentrated solution, will usually show quite different viscosities at 1 per cent concentration or less, while a given sample of secondary acetate washed in one instance with distilled water and in another with hard water will yield concentrated solutions of distinctly different viscosities. Although these differences are probably of relatively little significance to lacquer formulators, they are factors which must be carefully watched in research investigations.

In addition to the conventional methods of estimating molecular weights described above, a new procedure based on light-scattering produced by large molecules is coming into rather widespread use. This method is based on theoretical considerations developed by P. Debye and, for the first time, affords a means of determining molecular weights without the inaccuracies which result from the presence of low molecular weight fractions.

Molecular Weight Distribution. It should be observed that, except for determinations based on light scattering, all of these methods give the average molecular weight of the substance under investigation. Most resinous substances are constituted of a mixture of similar molecules of varying size. If the variation is great, then the average molecular weight gives relatively little information concerning the magnitude of the individual molecules present. It should also be emphasized that a small weight percentage of very low molecular weight material represents a relatively large molecular ratio, particularly where the range in molecular weight is wide. This statement also holds for small amounts of such impurities as water or solvents and has frequently been the source of griev-

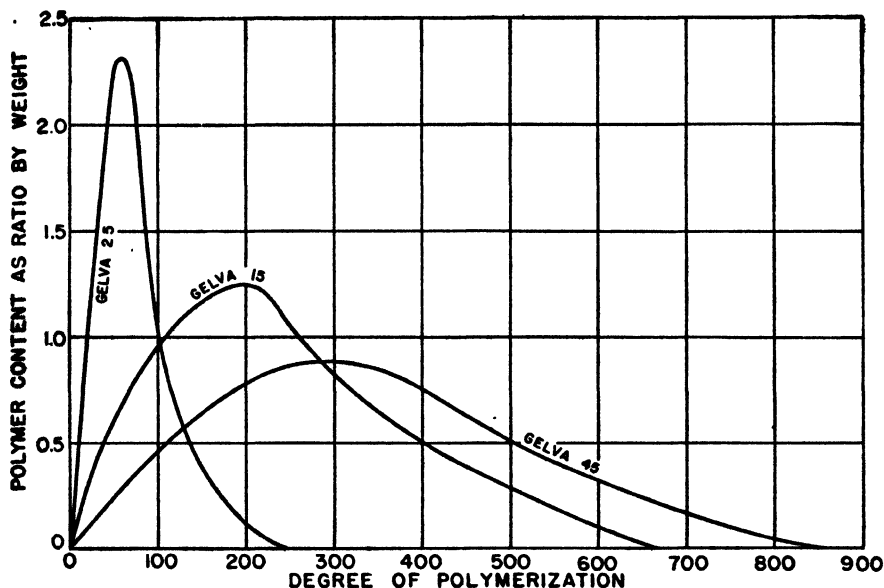


Figure 10. Weight average molecular weight distribution curves for three commercial grades of polyvinyl acetate. (Blease and Tuckett¹)

ous experimental error. For accurate information, therefore, a resin must be fractionated by precipitation, solution, or some other method and thus separated into carefully dried and solvent-free portions which are approximately homogeneous in molecular size. Fractionation, combined with molecular weight determinations upon each fraction, gives a knowledge of the molecular weight distribution in a given resin. Figure 10 shows distribution curves determined for commercial samples of polyvinyl acetate of three different viscosity grades.

Where the molecular weight of the fraction under investigation is substantially homogeneous, the value found experimentally should be the same, regardless of method—provided, of course, that the particular means of measurement is applicable to a high polymer of the size and shape at hand. Where there is a considerable spread, however, in molecular weight distribution of the sample investigated, the value obtained is an average of the molecular weights of all component fractions. Most of the procedures discussed, such as cryoscopic, ebullioscopic, osmometric, and end group methods, give average values which are dependent upon the mole fraction distribution in a polymeric mixture. Viscosimetric methods, however, yield average values which are dependent upon the actual weight distribution in such a mixture. The former average value is con-

tingent upon the number of molecules of different weights present in a given sample and is called the number average molecular weight. The latter average value being contingent upon weight distribution of the various fractions is known as the weight average molecular weight. The greater the spread in molecular weight distribution, the greater is the divergence between these two values which are absolutely equivalent only in a homogeneous fraction.

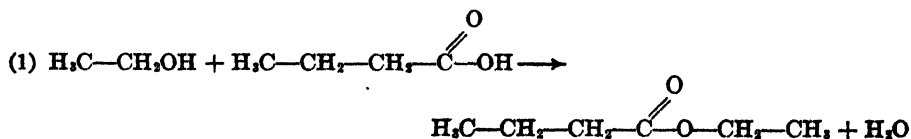
General Processes of Resinification

We have seen in a very general manner the ways in which physical and chemical properties and commercial utilization of resinous materials are related to the architecture of large molecular species. How are such large molecules formed?

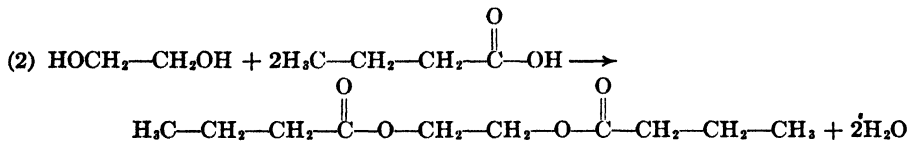
Why should the organic chemist obtain fairly simple, low molecular weight compounds on numerous occasions and yet, on others, produce materials of such large molecular dimensions, that, at times, they become almost distinguishable by the electron microscope? The answer to this and many other questions posed by the study of high polymers has not yet been given with certainty. Many important articles have been contributed to the literature and a number of invaluable books have sought to explain these problems by physical and mathematical discussions. Unfortunately, much of this vast accumulation of information is still rather speculative. Because of the uncertainty which surrounds many of these theoretical discussions, this text will make no pretense of considering any of them in detail. One is tempted to quote the genial Frenchman, Robert Lespieau: "Certain clans of investigators have contracted the habit of bluffing in an extraordinary way. They base extremely beautiful systems upon measurements which agree to about 400 per cent."

Resinification reactions are separated into two principal categories: condensation and polymerization.

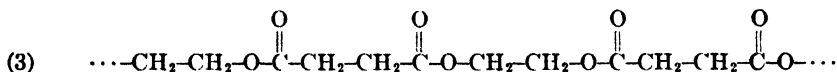
Condensation. In condensation reactions, water or some other relatively simple compound, usually of inorganic nature, is eliminated by reaction of two or more organic chemicals. Reactions of this type are common synthetic processes in the production of conventional low molecular weight organic compounds. For example, in the preparation of ethyl butyrate by esterification of ethyl alcohol and butyric acid, water is eliminated in accordance with equation (1).



If the alcohol contains two hydroxyl groups instead of one, *e.g.*, ethylene glycol, the resultant ester is still of low molecular weight:



If, however, the acid contains two carboxyl groups while the alcohol is dihydric also, the product is no longer of low molecular weight, but is a complex condensation product. The reaction is the same as above, but there is no well-defined point at which esterification must cease and the product is therefore a chain of considerable length, a portion of which is represented by formula (3)

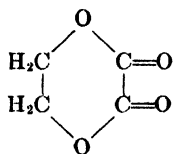


The precise point at which esterification ceases in the production of a prolonged chain like that just illustrated is determined in part by reaction conditions and in part by the specific nature of the reactants. Relatively little is yet known as to how or why such condensation reactions stop. The product being of high molecular weight—usually at least several thousand—it is more or less resinous in character. It belongs to the general category of condensation resins.

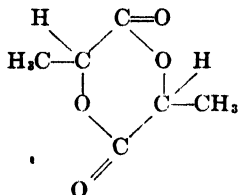
Resinification by condensation which has been illustrated here with esters may be carried out with numerous other organic compounds. In general, the formation of high molecular weight compounds will occur in condensation reactions where each of the two interacting chemicals contains at least two reactive, *i.e.*, functional groups, per molecule. For example, ethyl chloride and sodium sulfide can be reacted to form diethyl sulfide, but ethylene dichloride and sodium polysulfide react to yield "Thiokol A," a product of high molecular weight. Numerous cases of high polymer formation by condensation will be given in subsequent chapters.

It should be noted, in passing, that the formation of high molecular weight products by reaction of bi- or polyfunctional compounds with each other is the rule, rather than the exception. The production of conventional low molecular weight organic compounds by such reactions, although well known, is less common. Because of the historical interest of chemists in products which could be easily purified by crystallization or distillation, the exceptions to this general rule were better known than the rule itself, until very recent years. Illustrations of the preparation of low molecular weight compounds by polycondensation reactions will be

cited in later chapters. Where 5- or 6-membered rings can be produced in such operations, they are often formed, ethylene oxalate,

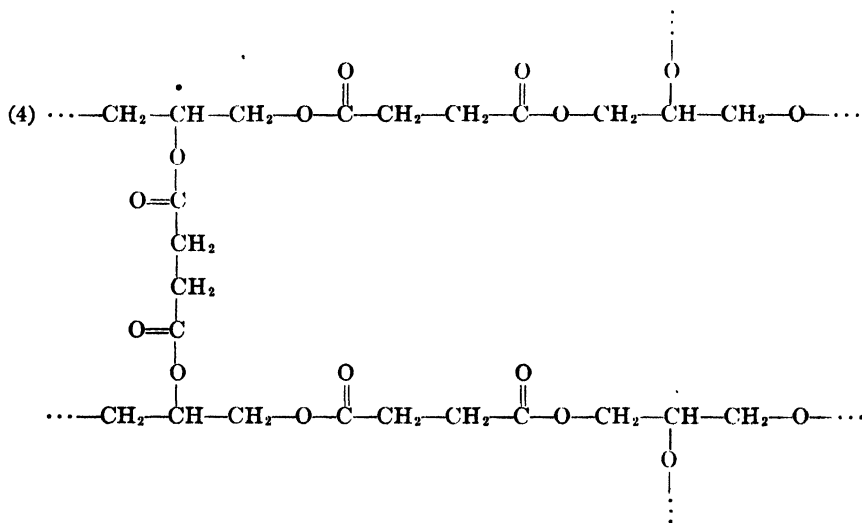


, and lactide,



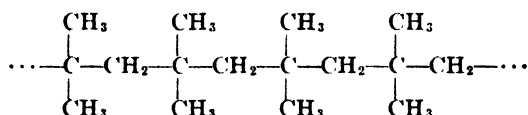
, being typical.

The examples of high molecular weight compounds made by condensation reactions which have been shown above are all linear and therefore thermoplastic. It will be apparent that if one, at least of the reactants possesses more than two functional groups, cross-linkages can be established between the principal chains and tridimensionality, with attendant thermohardened characteristics, is thus developed. If glycerol is used instead of ethylene glycol in the product shown in (3), then a complicated interlocked network results which may be represented in part as follows:



A considerable number of commercial plastics produced by condensation are thermoplastic, for example: nylon, some of the alkyds, some of the phenolics, thioplasts, and toluene sulfonamide-formaldehyde resins. On the other hand, the most important thermosetting plastics are also produced by condensation reactions, *i.e.*, the phenolics, ureas, melamines, and many of the alkyds. Fundamentally, the distinction between these two major classes from the synthetic point of view lies in the number of available reactive groups in each of the interacting component substances.

Polymerization. It has been noted above that another general type of resinification reaction is known: polymerization. In the latter, a high molecular weight compound is formed by consecutive addition of one unsaturated molecule to another across the double or triple bond without elimination of any substance by metathesis. Formation of low molecular weight compounds by polymerization is well-known. Dimerization of isobutylene to a mixture of C_8 olefins is an important commercial example of this process. So also is dimerization of acetylene to vinyl acetylene, an essential intermediate in the manufacture of neoprene. In both of these instances, however, the formation of dimer from monomer is only one of many polymerization reactions which each of these unsaturates is capable of undergoing. Careful selection of reaction conditions is essential to assure formation of dimer rather than higher polymers. In the case of isobutylene, for example, addition of one molecule to another across the double bond may occur until products having a molecular weight of 200,000 or more are obtained. A portion of the structure of such a polyisobutylene may be represented as follows:



In the case of acetylene under certain reaction conditions, cuprene—an insoluble, apparently tridimensional, solid, brown, voluminous powder of general formula $(C_2H_2)_x$, but of unknown structure—is produced.

Ordinarily the catalysts and reaction conditions required for low and high polymer formation differ. Moreover, the production of high polymers does not often proceed through intermediate lower members of the same polymeric series; at least low members such as dimers and trimers cannot usually be isolated from reaction mixtures in which high molecular weight polymers are being produced. It is also not often possible to polymerize further a high polymer once reaction has stopped, neither can dimers or trimers often be converted to the same high polymers as would have been obtained directly from the monomer. Numerous hypotheses have been advanced to explain these facts. The most popular one at the present time is a development of the theory of chain reactions, the double bond of a monomer being supposedly activated by some means, probably by the polymerization catalyst. Another unsaturated molecule adds across the activated group and the activation is transmitted to the unsaturation present in this additive compound. This reaction continues consecutively and with great speed until the molecule becomes deactivated by some means, whereupon the chain is interrupted and polymerization

ceases. This type of polymerization is illustrated specifically in the case of polystyrene (see Chapter 16).

Some unsaturated systems can be polymerized very easily to high molecular weight compounds. Other unsaturates appear less amenable to this type of reaction. Many rules have been enunciated to predict and explain the tendencies of unsaturated systems to polymerize. With each new day, however, compounds formerly thought to be incapable of polymerization are polymerized so that most speculation of this kind will be omitted from this text, discussion in the following chapters being confined largely to unsaturates which are actually polymerized commercially to useful compounds.

It should be noted that high polymers are frequently produced by conjoint polymerization of two or more unsaturates, in which case the monomeric units of each appear in the polymer. The resins thus produced are known as copolymers. Many commercial products of this kind are of great importance, especially among the vinyl resins.

In some instances, an unsaturated compound which, alone, cannot be polymerized does lend itself to conjoint polymerization with other readily polymerizable unsaturates. Maleic anhydride and styrene are a case in point. Polymers so made are often termed heteropolymers.

Ordinarily, polymerization of an unsaturated compound leads to the formation of a molecule possessing a linear skeleton. In some instances, however, for reasons which are not yet clear, branching of the chain appears to occur. The more complicated the branching, the more a polymer of this kind tends to resemble a cross-linked, thermohardened plastic.

Where two unsaturated groups are present in a single monomer, the possibility exists that each will enter into polymerization reactions, resulting in formation of a cross-linked, thermohardened plastic. Copolymers of styrene and divinyl benzene and polymers of diallyl phthalate are typical of this type of resin.

The fundamental characteristic of high molecular weight compounds formed by either condensation or polymerization is the repetition of one or more unit groups a very large number of times. In the case of polymerization, the unit group has the same formula as the monomer; in the case of condensation, it lacks the elements of water or some other simple substance removed during reaction. The number of times that the unit group is repeated in a polymer is known as the degree of polymerization, or D.P. of the latter. Carothers has suggested that all of these high molecular weight compounds should be called polymers, the two categories being distinguished as condensation or C-polymers and addition or A-polymers. He called the unit group of either type of polymer a "mer."

Within the past few years a considerable number of mixed condensa-

tion-addition polymers and copolymers have become important commercial articles. "Laminac" and several other low-pressure, no-pressure laminating resins are cases in point.

Relation of Chemical Nature to Properties

We have seen earlier that the geometrical structure and the size of high polymeric molecules exercise important influences upon their behavior. A third factor which contributes to the physical and chemical behavior of these materials is, of course, the chemical nature of substituent groups which they contain. One very significant physical property which is influenced by these groups is solubility. In general, the rule that like dissolves like applies as well to resins as to other bodies. The presence of hydrophilic groups like the hydroxyl or carboxyl radical increases oil resistance but decreases water resistance. Where many groups of this kind are present in a single molecule, as in polyvinyl alcohol or polymethacrylic acid, the resin may be soluble in water. Non-polar groups, such as alkyl and aryl radicals decrease oil resistance and increase solubility in common solvents while increasing water resistance. Sulfur as sulfide or polysulfide increases water resistance and moisture impermeability. Electrical properties are best in materials of hydrocarbon nature. Abrasion resistance appears to be affected to some extent by chemical nature, being often decreased by alkyl groups and increased by hydroxyl radicals. Oxidation resistance and hence aging characteristics are improved as saturation of the molecule increases.

It should again be emphasized that much of our knowledge concerning the chemistry of high polymers is still open to question. The generalizations which have been enunciated in this chapter are neither all-inclusive nor perfect, but they serve as useful aids to the classification of our present information in this field which will be discussed more in detail as we consider individual families of plastics.

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Chapter 5

Mechanical Manipulation of Plastics — Molding

The innumerable commercial articles into which synthetic resins and plastics are fabricated can be grouped as follows:

1. Molded forms
2. Laminated shapes
3. Molded laminates
4. Plywood
5. Cast objects
6. Extruded shapes
7. Sheets, sheeting, and foil
8. Blown goods and allied products
9. Spun filaments
10. Surface coatings
11. Resin-treated fabrics and paper
12. Adhesives
13. Miscellaneous goods

Often there are several ways in which members of each of these classes can be produced. In the case of high-pressure molding, for example, plastics may be formed by compression, transfer, jet, or injection processes, depending upon the material and the application.

We have seen that plastics are classified in two main groups according to their chemical behavior: thermoplastic and thermosetting. This typing according to performance upon application of heat is far from a purely theoretical consideration. It is a matter of vital importance to every molder and fabricator, for it imposes very definite restrictions upon the way in which a given plastic can be handled.

Because the physical properties of synthetic resins are largely defined by such chemical characteristics as their molecular shape, weight, and functional radicals, those plastics which possess certain molecular properties in common can be fabricated by similar methods. Hence a given operational process is applicable to numerous plastics, with only minor variations of detail. In this chapter we shall consider briefly the general ways in which synthetic resins and plastics are manipulated in making the diverse products listed above.

MOLDED ARTICLES

Many plastics can be shaped in a mold, with the application of heat and pressure, to yield such articles as buttons and bottle closures, pipe-stems and cigarette cases, radio cabinets and vacuum cleaner hoods, light reflectors and hairbrush handles, combs and costume jewelry, sub-machine gun stocks and airplane antenna stanchions. Thousands of molded ar-



Courtesy Bakelite Corp.

Figure 11. Battery of tumbling barrels for removing flash from molded plastic objects.

ticles of the greatest variety are turned out daily by the presses of the many custom molders throughout the country.

In manufacturing the majority of products of this kind, plastics are utilized in the form of molding compounds, often called molding powders, which are intimate mixtures of resins and other materials added to impart certain desirable physical properties, to facilitate molding operations, or to reduce cost. Ordinarily a molding powder is a granular mass of particle size varying from that of a fine talcum powder to pieces as large as peas. Where the nature of the filler permits, compression molding compounds are relatively fine. Usually they will pass through a 14 mesh screen although long fiber fillers and chopped fabric oblige greater coarseness. Injection molding compounds are much larger in particle size, being called 3/16 inch granules.

Numerous finishing operations which will not be discussed in this text are applied to molded articles after removal from the die. Elimination of flash or fins from compression molded articles and of sprue, runners, and gates from injection molded pieces is carried out in several ways, often with the use of tumbling barrels in the case of small objects. Buffing and polishing, etching, sand-blasting, grinding, machining, cementing, and mechanical attachment of various molded parts are operations important to the fabricator of finished plastic objects. The surfaces of molded plastics are also sometimes altered by such processes as painting or electroplating.

Molding of Thermosetting Plastics

A thermosetting resin is one which, upon heating, softens or perhaps melts, but upon further heating develops a complex, cross-linked, tridimensional structure and solidifies to a hard, insoluble, infusible mass that no longer softens appreciably below its temperature of decomposition. Because of this behavior, such a plastic can be shaped by filling a suitable mold with powder, closing while simultaneously applying heat and pressure, and finally releasing the pressure after a sufficient length of time has elapsed to set or cure it chemically. Thermosetting resins can be ejected from a hot mold, after curing, without fear of serious distortion if reasonable care in handling is exercised for a few minutes after removal. This fact permits rapid molding and was one of the factors accounting for the popularity of thermosetting resins in preference to thermoplastics before the development of injection molding methods.

The practical value of a thermosetting resin is determined not only by the physical and chemical properties of the finished plastic and its cost, but also by the time and temperature required for cure and by the ease with which it flows in the mold to give faithful reproduction of minute detail without blemish. Depending upon the size and shape of the article to be produced, most thermosetting plastics are cured in 30 seconds to 12 minutes. Pressure is employed in order to make the semi-fluid mass conform quickly and accurately to the shape of the mold in which it is set and to hold the shape during the curing reaction when gases and water vapor form inside the piece. If this reaction is not completed under pressure, blemishes will form. In the latter respect, especially, high-pressure molding differs markedly from low-pressure techniques in which non-gassing resins are utilized. This introduces other conditions which thermosetting resins must fulfill in order to serve as components of molding powders: they must cure well and quickly under pressure and should not require cooling in the mold. In some instances, thermosetting resins decompose where heated in a confined space. Such behavior is particu-

larly characteristic of the alkyds—resins which are extremely valuable, however, in surface coatings. Obviously such decomposition rules them out for use in molding powders. In other cases, as with the ureas, free-flowing properties are not fully developed by heat alone, and pressure must be applied throughout the molding cycle in order to obtain sufficient fluidity to yield perfect moldings.

Properly cured thermoset plastics are insoluble in common solvents. By comparison with thermoplastics they are resistant to heat. Hence, save for warpage and effects of weathering and aging, they will retain their shape indefinitely and are not altered by atmospheric temperature fluctuations. Nevertheless, although properly designed articles molded from thermosetting resins are dimensionally relatively stable, they are by no means warp-proof. Warpage may be caused by gradual release of strains molded in during the process of fabrication (principally due to the presence of unequal cross-sections), by change in the moisture content of the molded article resulting from moisture initially present in the molding powder, by fluctuation of the humidity of the atmosphere to which the article is exposed, and by gradual and progressive chemical change of an incompletely cured article. The first of these causes of warpage can be minimized by care in designing and molding and, to some extent, by subsequent heat-treatment. The second factor can be eliminated by care in storage and by pre-heating the molding powder before fabrication. The third effect must be considered in selecting the right kind of plastic for a given job. The fourth cause of warpage listed above can be easily eliminated by careful control of the molding cycle. There may, at times, be a temptation for a custom molder to undercure moldings in his own best interests for the sake of minimum cycles and maximum production volume, but this practice is often false economy because of subsequent warpage. Heat treatment after molding advances the resin farther into the C-stage and thus also helps to eliminate warpage caused by inadequate cure.

Preparation of Molding Compounds. There are three commercially important types of thermosetting resins currently available as molding powders—the phenolics, ureas, and melamines. They are manufactured by reacting a phenol, urea, or melamine, respectively, with formaldehyde. There is no clean-cut point at which these reactions can be stopped with assurance that the products have been advanced to the same state of resinification from batch to batch and are at the proper point for fabrication of molding compound of certain standard specifications, so that the arts of reaction control and batch mixing are important for the establishment of uniformity of manufactured products.

After preparation of the resin itself, other ingredients of the molding

compound are mechanically combined therewith, either on a rubber mill or in a ball mill as a dry mix. Careful control is maintained over each batch, usually by means of sample moldings, in order to preserve uniform flow characteristics. After the materials are sufficiently mixed on the rolls to insure homogeneity, the material removed therefrom is chopped in a hammer mill or other attrition device and a large number of batches are blended together in a suitable machine. The final product of the blender is used for molding or pre-forming purposes.

Almost all commercial molding compounds of the thermosetting category are mixtures of synthetic resins with fillers, coloring materials (usually pigments), and small amounts of other substances which may complete or hasten cure, or which may lubricate the mold or material thus facilitating removal of the finished article. Thermosetting molding powders rarely contain much over 50 per cent of resin. The remainder consists of 40–45 per cent filler, up to 5 per cent coloring matter, and up to 1 per cent mold lubricant.

The utilization of fillers in the manufacture of molding compounds often reduces the cost of the latter, but it may at times increase it. Economy is never the sole objective. Fillers always improve one or more properties of the finished molded plastic. In the case of the phenolics, the most common filler is finely divided wood flour. Cotton flock, mica, asbestos, and numerous other products are used for special purposes. Purified *alpha* cellulose is an essential filler for the ureas.

Thermosetting molding compounds are usually sold, ready made, by plastics manufacturers to custom molders. The latter then fabricate the finished shaped articles by one of three general methods: (1) Compression molding. (2) Transfer molding. (3) Jet molding.

Compression Molding. Compression molding is the oldest and most common method. In this process, the female portion of the mold is filled with approximately the necessary amount of molding powder, closed with the male portion, and the molding operation effected in a hydraulic press under elevated heat and pressure. General conditions used to compress mold the three main types of commercial thermosetting plastics are as follows:

Plastic	Compression Molding Pressure (lbs per sq in)	Compression Molding Temperature (° F)
Phenolics	2000–8000	280–360
Ureas	1500–6000	290–325
Melamines	1500–6000	300–330

Molding is carried out by hand operated, semi-automatic, or fully automatic presses, depending upon the equipment at hand, the nature of the article to be made, and the number of units per day required by the pro-

duction schedule. Regardless of the type of press, the same series of operations must be carried out, either by hand or automatically. The mold is loaded, closed, held under pressure at the required temperature for the necessary length of time, then opened, the piece removed from the mold, and the latter blown out ready for repetition of the cycle. Often



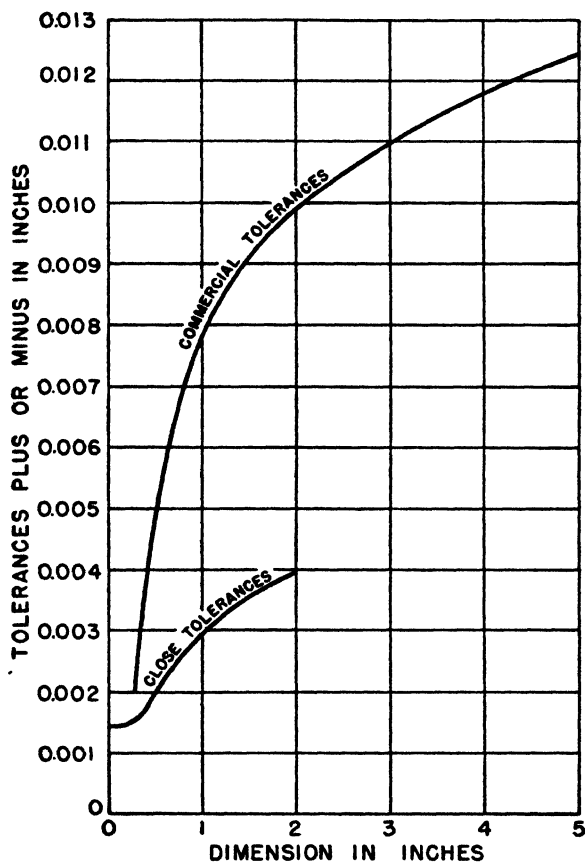
Figure 12. Seventy-five ton semi-automatic press with positive mold.

Courtesy Boonton Molding Co.

it is desirable to breathe, *i.e.*, close the heated mold momentarily and then reopen it to allow escape of any occluded gas before it is finally closed and held shut for the length of time required to cure the plastic. In precision operations, the mold is sometimes cooled before removal of the finished article to insure good dimensional tolerance and stability.

In fully automatic machines, molding powder is dumped into a hopper at the top and the molded articles come out at the bottom, all opera-

tions following each other in the necessary sequence by mechanical control. Bottle caps, ash trays, and simple electrical parts, for example, produced in large volume without metal inserts are usually molded in automatic machines. The use of metal inserts ordinarily requires hand



Courtesy Westinghouse Electric & Manufacturing Co.⁴⁹

Figure 13. Tolerances for molded phenoplasts

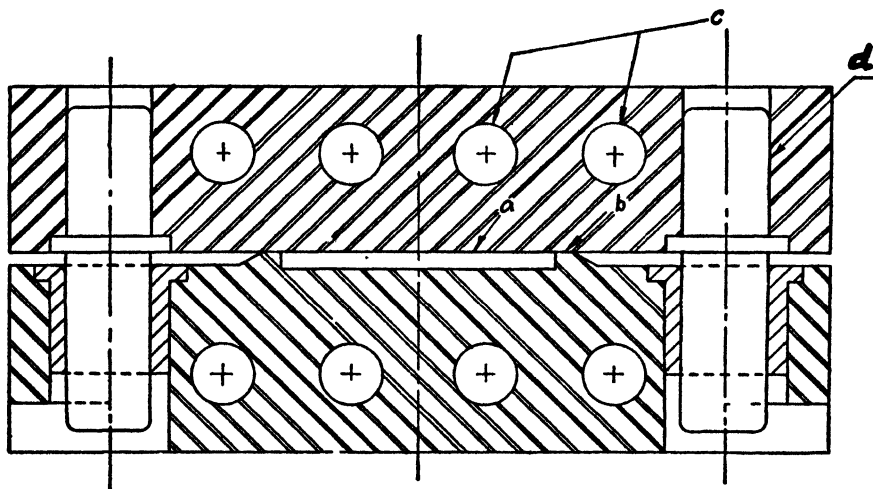
assembly in the mold, hence only semi-automatic machines can be used in such cases.

Molding tolerances for phenoplasts are shown in Figure 13.

Compression Mold Design. Mold design is a matter of extreme importance, for improper design may lead not only to unsatisfactory performance of the molded piece, but it may spell the difference between success or failure on a cost-per-part basis.

Depending upon the complexity of the molded article, the required pro-

duction schedule, and the number of presses to be used in meeting it, any of several different types of mold design may be used: flash, positive, or semi-positive. The cavity may consist of a single piece, or it may be a split mold, built up of two or more parts fitting together within an outer chase. It may sometimes have additional loose parts within it. It may be a single cavity or multiple cavity type. In the latter case, or if several molds are to be made of a given design, they may be machined separately, often with the aid of a duplicator, or they may be hobbled, in which case



Courtesy Plaskon Division, L.—O.—F. Glass Co.³⁸

Figure 14. Full flash mold.

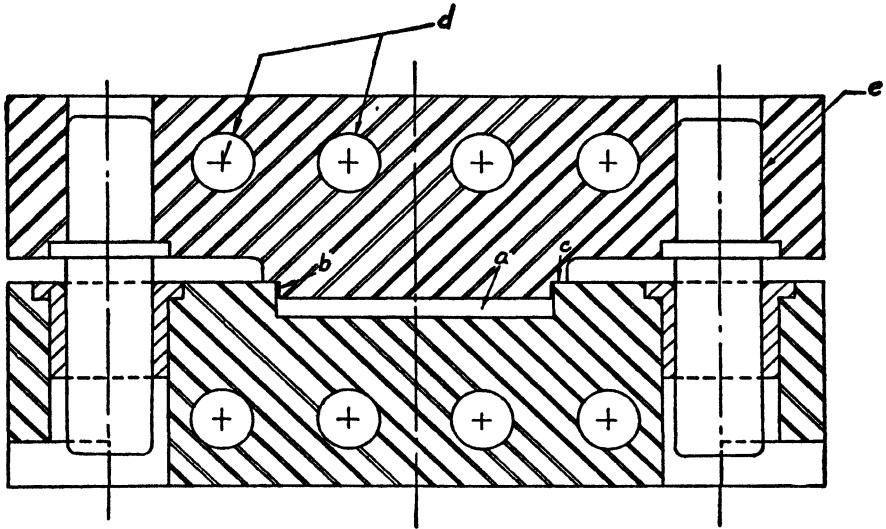
(a) Mold cavity. (b) Overflow or "land" area. (c) Coring for steam heat. (d) Guide pins to prevent shifting in relative positions of top or force plate and bottom or cavity plate.

a master is first produced, in the form of the finished piece, of especially high-grade tool steel. Duplicate dies are then subsequently hobbled in machine steel and case-hardened.

The fundamental differences between flash, semi-positive, and positive molds are illustrated in Figures 14 to 16. The design of a mold of each of these three types is shown in the order given, the article being similarly shaped in each case.

Many minor variations of each of these types are used and designated by special diemakers' terms.

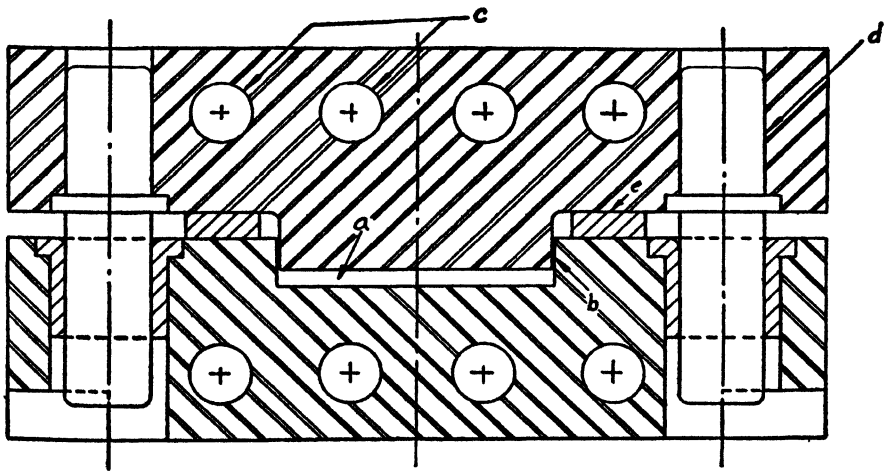
In the flash type mold, an excess of material, usually some 3 per cent, is charged into the cavity and, upon closing, is squeezed out as horizontal flash. Once the mold is completely closed, its contents are no longer under positive pressure. In the positive mold, on the other hand, continu-



Courtesy Plaskon Division, L.—O.—F. Glass Co.³⁸

Figure 15. Semi-positive mold.

(a) Mold cavity. (b) Vertical or positive type flash. (c) Horizontal or flash type cut-off. (d) Coring for steam heat. (e) Guide pins.



Courtesy Plaskon Division, L.—O.—F. Glass Co.³⁸

Figure 16. Positive mold.

(a) Mold cavity. (b) Vertical flash. (c) Coring for steam heat. (d) Guide pin. (e) Land.

ous positive pressure is applied as long as the mold is closed. Such a mold requires accurate weighing of the charge unless a loose fit between plunger and cavity allows excess vertical flash and the plunger is landed by outside stops.

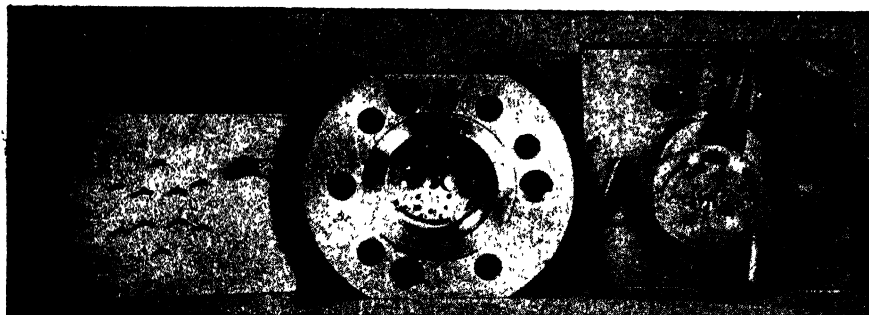
The semi-positive mold is a combination of flash and positive types, so that positive pressure is maintained without the necessity for such accurate weighing.

The design of an article to be molded from a plastic and the construction of a suitable mold are highly technical problems requiring the attention of an engineer or draftsman thoroughly conversant with molding technique. A prospective customer should never attempt completion of the design of a molded article without consulting his molder's engineers. It is, for example, only rarely possible to reproduce exactly in plastics the shape of an article formerly made of metal. Square corners should be avoided to prevent sticking to the mold and nicking of the finished article upon removal therefrom. Taper of wall thickness in articles of long draft is desirable in order to keep the plastic constantly under pressure as it flows upward into zones of restricted cross-section. Undercuts should be avoided, for although they can occasionally be introduced by use of a split mold, such molds are often impractical and exorbitantly expensive to manufacture and use, because they require hand assembly in each molding cycle. The cross-sectional thickness should be maintained as nearly uniform as possible throughout the piece. This makes for better flow and homogeneity of composition and cure. Thin sections, less than about 0.05 inch, should be avoided in order to prevent warpage. When the molded article will be subjected to shock or vibration, or when high dimensional stability is required, ribbed reinforcements may be necessary for proper design.

Metal inserts are frequently used in combination with molded plastics. In compression molding their use is limited by the desirability of aligning them in such a way that their axes will be parallel to the direction of molding, *i.e.*, at right angles to the surface of the press platens. This provision is frequently necessary in order to avoid displacement during molding.

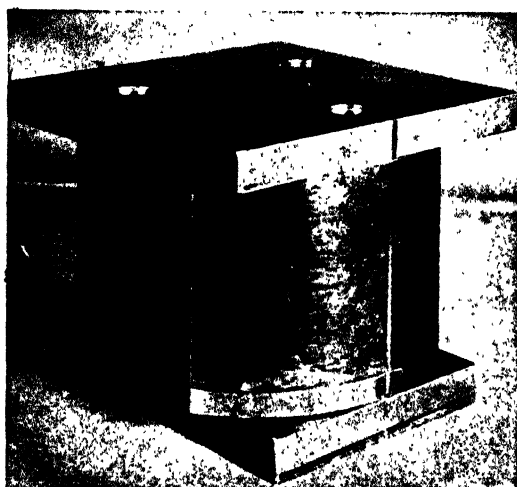
Construction of molds for consumer goods to be made of plastics often permits advantageous use of modern theories of functional and streamline design which not only facilitates molding, but also enhances eye-appeal at the point of sales. Hence, it is frequently desirable for a prospective plastics user to draw upon the services of an industrial designer.

In planning a mold for a given plastic, it is essential to know the bulk factor of the molding powder to be used, that is to say, it is necessary to know what volume decrease will occur during molding. The term

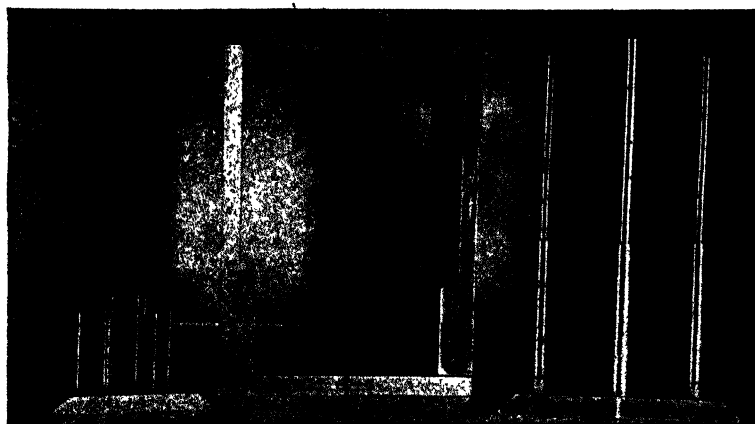


Courtesy Pittsburgh Equitable Meter Div., Rockwell Mfg. Co.

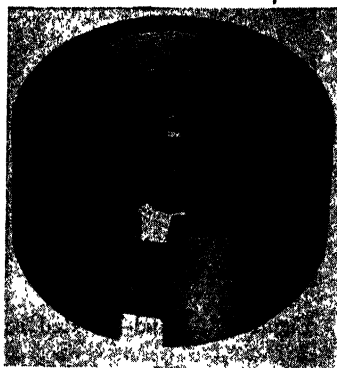
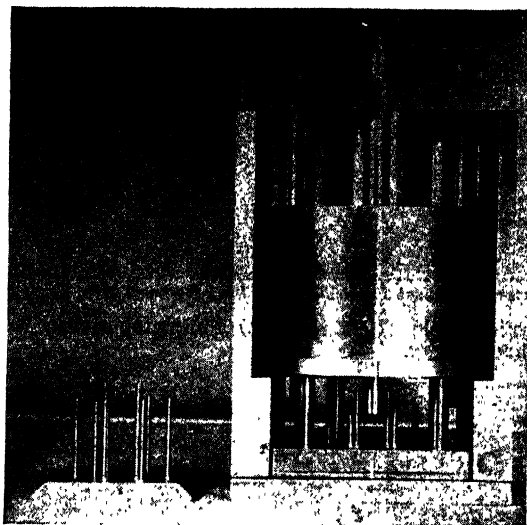
Figure 17. Hand-operated compression mold. (left to right) Pin-plate, cavity, and plunger.



Assembled mold.



Knockout devices.



(left) Mold disassembled.

(above) Molded article.

See also Figures 73 to 78, Chapter 7, for further illustration of compression molding principles.)

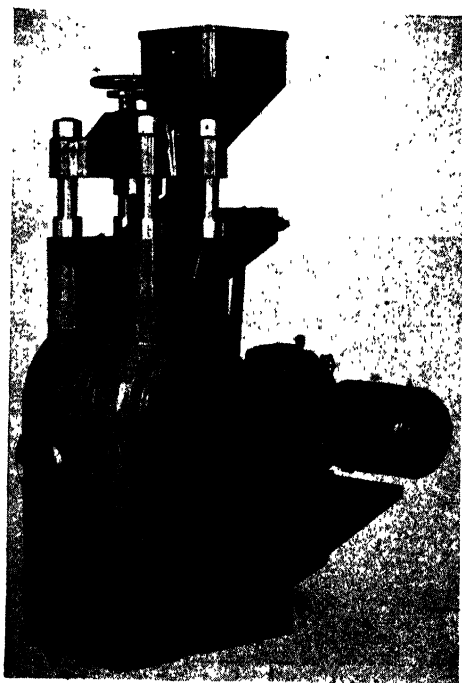


Figure 18. Plastic preform press built especially for precision plastic preform work.

Courtesy Defiance Machine Works, Inc.

bulk factor signifies the ratio of the volume of molding compound to that of molded article produced therefrom. This value differs from one molding compound to another, even of similar plastics.

Another factor which must be known in order to design a mold for a given plastic is the amount which the latter will contract in cooling to room temperature after removal from the hot mold. Both bulk and



Figure 19. Rotary preforming press.

Courtesy Boonton Molding Co.

shrinkage factors are reported by plastics manufacturers for their various products.

Many molding powders are produced in several degrees of plasticity; the lower the plasticity, the higher the temperature and pressure required and the more rapid the cure. Low plasticity molding compounds give the highest quality moldings at the greatest possible rate of production, but they cannot always be used, for the design of the article to be molded influences the selection of plasticity of molding compound. In general, the larger the article, the longer the draft, and the thicker the piece, the greater must be its plasticity.

Average molding conditions for the three main classes of thermoset-

ting resins have been given above. In order to withstand the pressures required and at the same time afford a polished die surface which will not be blemished by repeated use, it is essential to machine the molds from high grade tool steel, to surface harden them, or to chromium plate them. The selection of suitable alloys and hardening methods is a matter requiring care and experience on the part of the molder.



Courtesy Bakelite Corp.

Figure 20. Feeding phenolic molding powder to hopper of rotary preforming machine.

Tableting and Preforming. In compression operations, recourse is often had to tableting and preforming in order to speed up molding. These expedients are well defined by their names. Molding powder is compressed at room temperature into the form of more dense tablets or larger pills or preforms. In some cases, as with chopped impregnated duck, the preform may approximate the final shape. Tablets and preforms fit freely inside the mold ultimately employed. The bulk factor of a molding powder may be more than halved by such methods. The purpose of preforming is usually three-fold: accuracy of weight, cheapness of creating that

weight, and ease of handling. The ease with which tableting and preforming can be carried out depends largely upon the nature of the resin, the type of filler, and the temperature. It is often unsuccessful where chilled, or even at room temperature.

The character of the filler is especially important. Wood flour and powdered mica facilitate automatic preforming. Pulp-resin innovations,



Courtesy The Girdler Corp.

Figure 21. "Thermex" high frequency dielectric heating unit employed in curing plywood cylinders.

especially in the case of phenolic resins, have made practicable the preforming of certain types of materials filled with long fibers, especially kraft pulp. The resin and pulp are mixed in an aqueous slurry. Suction is then applied, often through a wire mesh of the desired shape. Preforms are thus formed over the mesh directly from the slurry in much the same manner and, indeed, by one manufacturer with the same equipment as is utilized in the fabrication of paper pie-plates. After drying, the preforms

are ready for molding. Both shaped articles and flat boards can be made in this way. The latter can subsequently be molded into simple shapes or used as reinforcing inserts in compression molded articles.

Long fiber fillers and chopped fabric are particularly difficult to preform and often require hand manipulation. In such cases, the material is weighed out by hand and compressed in a single cavity mold installed in an air press for the sake of rapidity.

Electronic Preheating. In compression molding, considerable time can be saved by preheating the molding powder or preforms. A very impor-



Courtesy The Girdler Corp.

Figure 22. Use of "Thermex" high frequency preheating equipment in plastics molding.

tant advance in preheating technique has been developed by the use of dielectric heating, also known under such names as electronic or "Heatronic" preheating. Several different manufacturers now produce equipment for carrying out this operation which has the great advantage of bringing the entire mass of the preform close to the molding temperature so quickly that little curing is begun. Much thicker pieces can thus be molded than by ordinary compression methods, for the entire body of the plastic is uniformly heated. The time required for heating in the mold is substantially reduced. Moreover, the danger of overcure of thin sections and undercure of thick ones is largely eliminated and articles of varying cross-sectional thickness can be safely produced. Because of these three factors, the versatility of compression molding has been greatly broad-

ened by the introduction of electronic preheating (see Figure 52, Chapter 6).

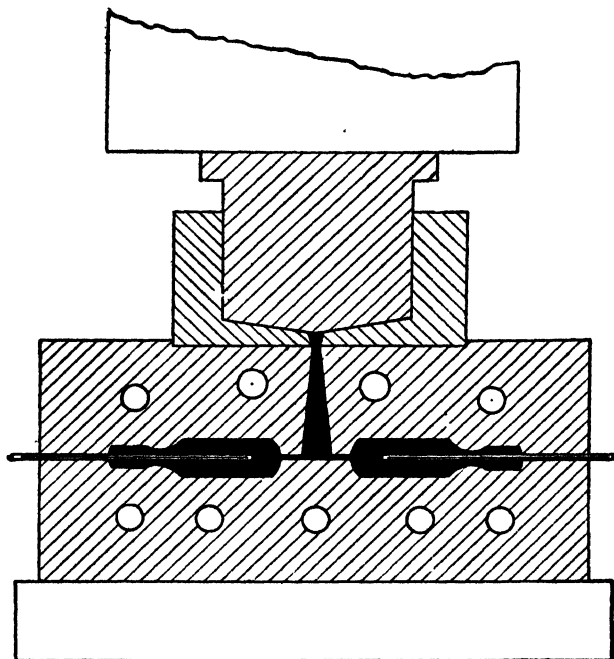
Transfer Molding. By far the greatest amount of molding of thermosetting plastics is done by conventional compression methods. During the past decade, however, another technique known as transfer molding has been developed. It was pioneered by the Shaw Insulator Company. To a certain extent it can be thought of as a combination of techniques of compression and injection molding. In transfer molding, a powder of especially high plasticity and, hence, of relatively long curing time and good flow characteristics, is heated or "plasticized" in an exterior chamber before it enters the mold. After the powder is heated sufficiently to become semi-fluid, it is forced through an orifice into a closed, heated mold where curing is completed by continued application of heat and pressure for the requisite length of time.

The plasticizing chamber is incorporated as a supplementary cavity in the upper part of the mold above the die. It is provided with its own force plug, while the mold itself is held closed throughout the operation. In molding, the powder is fed into the cavity in the upper part of the mold which is supported on the lower platen of a vertical hydraulic press of the kind used for compression molding. The molding compound is first heated until semi-fluid, then forced through one or more orifices in the bottom of the plasticizing chamber into the lower mold. Upon completion of the curing cycle, the mold is opened, the article removed, and the gate and sprue broken off and discarded. The mold is then closed again and the cycle repeated. The plasticizing chamber, therefore, has to be loaded by opening the press in each cycle. This constitutes an important difference from injection molding, as will be seen in the next section. The pressure used in transfer molding is usually much greater than in strict compression operations and may reach 10,000 pounds per square inch. Figure 23 illustrates the fundamental principles involved in transfer molding.

Transfer Mold Design. The design of the mold for transfer operations differs somewhat from that for compression molding. It must be provided not only with an upper plasticizing cavity, but since it is held closed throughout the molding cycle, it must be equipped with a satisfactory sprue through which the semi-fluid plastic mass can enter and, if more than one cavity is to be made, it must bear runners connecting them so as to assure uniform distribution of plastic. Particularly good heat distribution is essential throughout the mold and plasticizing chamber, otherwise over-curing may occur in the orifice with consequent jamming. The mold must be equipped with suitable knockout pins and with holes or pins to maintain any specified inserts in position. Some material remains

behind in the plasticizing chamber so that provision must be made for its removal.

The principal advantage of transfer molding is the opportunity it affords of molding especially complicated shapes, often with split molds, and of utilizing complex inserts. The plastic is already converted to the form of a heavy paste before it enters the mold cavity. Hence the insert is subject to hydraulic pressure, equal on all sides, until the mold is full



Courtesy Bakelite Corp.¹⁵

Figure 23. Diagrammatic sketch of principles involved in transfer molding process.

and the insert is supported uniformly. If inserts are sufficiently firmly emplaced to avoid displacement by the surge and swirl of plastic within the die, there is no directional tendency for them to be displaced, regardless of their shape or position in the mold. This is a very different situation from that which exists in compression molding, where unevenly distributed solid pressure is exerted against inserts by unheated, hard chunks of molding powder during the early stages of the operation. In compression molding, the axis of inserts is therefore preferably parallel to the direction of molding. If cross-inserts are molded by compression, more care must be exercised in applying pressure. Mold costs for transfer operations are frequently less than for compression molding.

Finishing costs are also often lower, although the necessity of discarding the cured sprue and residue in the plasticizing chamber may result in greater materials cost than in compression operations.

Improvement of physical properties is made through transfer molding

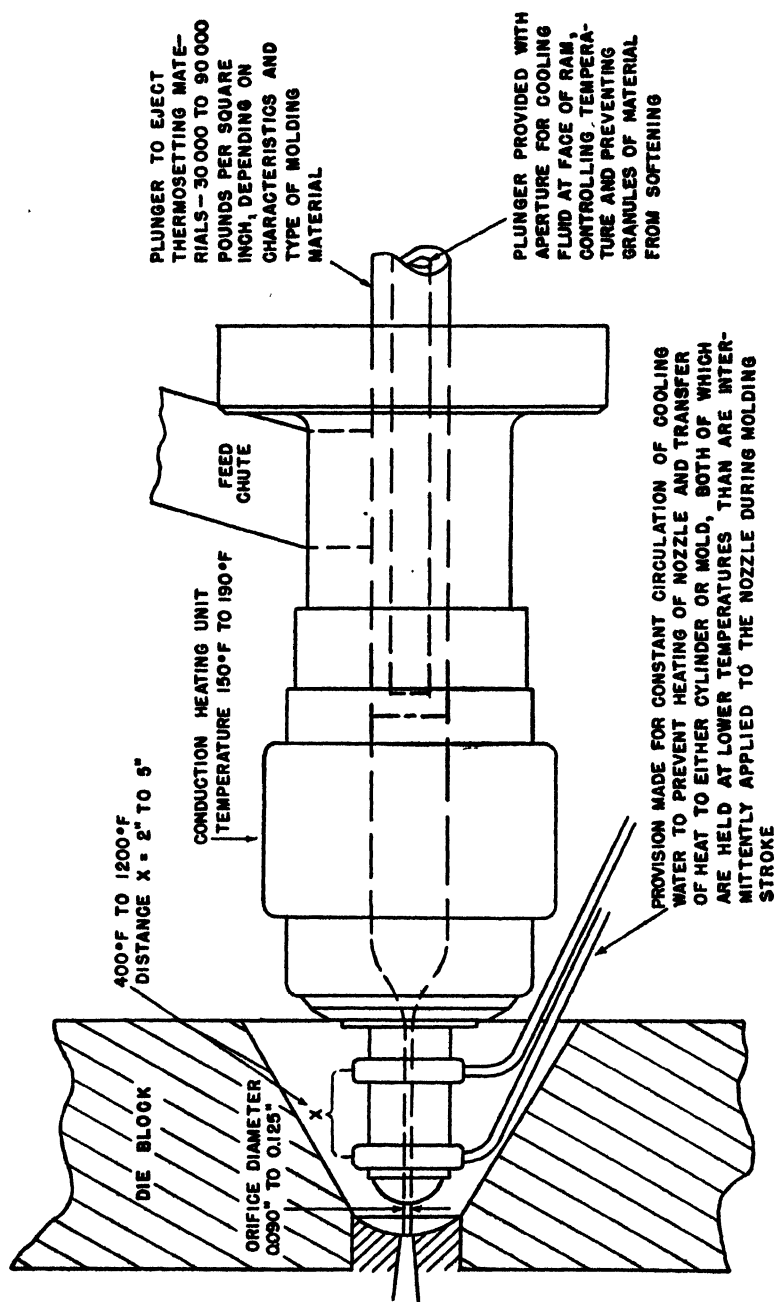


Courtesy Boonton Molding Co.

Figure 24. Single cavity transfer type hand mold—complicated piece.

by virtue of more thorough and uniform heating of the plastic. This is particularly true of molded pieces of more than $\frac{1}{4}$ inch thickness.

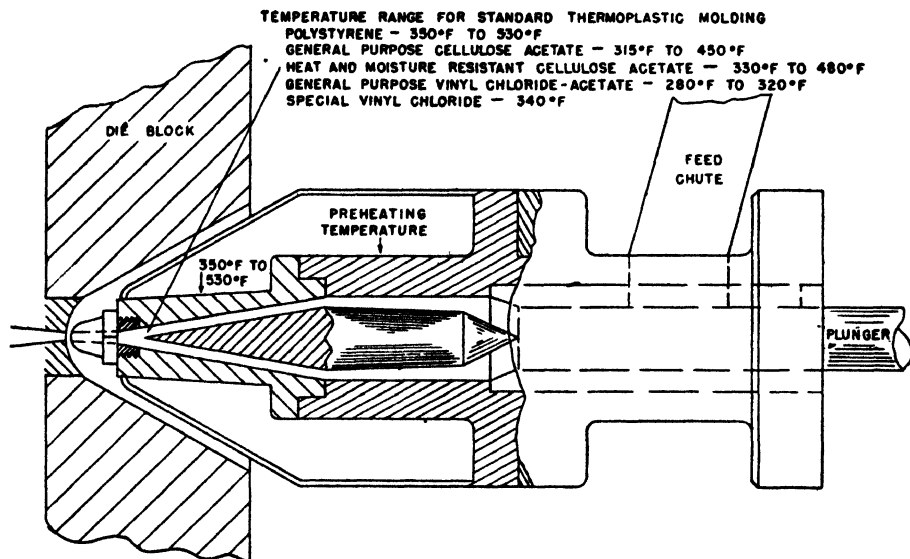
Jet Molding. The most recently developed method of molding thermosetting plastics is known as jet molding. This operation is truly an adaptation of injection methods to the handling of heat-curable resins. The fundamental principle is "plasticization" or softening of the material



Courtesy Bakelite Corp.

Figure 25. Jet molding nozzle principle used for thermosetting materials in conversion unit which can be adapted to standard fully automatic molding machines.

to be molded in an exterior chamber from which it is ejected by means of a moving plunger into a closed mold held at a sufficiently high temperature to bring about cure. Jet molding differs from injection molding, described later, mainly in details. As just mentioned, the mold temperature is high enough to effect cure of the resin. In order to permit ejection of filled plastics, even including chopped fabric filled materials, the torpedo, or spreader, located within the plasticizing chamber of injection molding machines is eliminated from the jet molding heater. In contrast to the injec-



Courtesy Bakelite Corp.

Figure 26. Typical injection molding nozzle principle used for thermoplastic materials.

tion molding process, also, the nozzle of jet molding equipment is so arranged that it can be alternately heated to a high temperature and then cooled with water. Thus, while material is entering the die, it is brought to a high temperature, but immediately after filling, the residual plastic in the nozzle is cooled to prevent curing and jamming of the orifice. The plunger of the jet molding machine is also equipped for water cooling in order to obviate scoring which might otherwise result from the close tolerances required. Special design of the runners and gates of the molds insures turbulent flow of plastic passing through them. Jet molding is adaptable to almost all types of thermosetting plastics and is being watched closely by the plastics industry. Figure 25 illustrates the fundamental principles of jet molding units and should be compared with Figure 26 showing conventional equipment used for injection molding of thermo-

plastics. Most injection molding machines can be converted to jet molding operations.

It should be added that jet molding is a tricky operation, at best, in its present state of development. Other objections to the process include limitations it imposes as to piece types, the high cost of slugs in proportion to usable material, and the relatively great investment in equipment as compared with transfer or compression molding.

Molding of Thermoplastics

A thermoplastic is a resinous material which, upon heating, softens or melts and remains in this condition until cooled. This operation can be repeated as often as desired with little or no alteration of its chemical or physical properties. In molding thermoplastics, therefore, it is necessary to retain the finished piece in the mold until it has cooled to such a temperature that it will no longer change shape when removed. If handled in a compression mold, this obviously requires alternate heating and cooling in every cycle, resulting in a prohibitive length of time to complete a single molding of complicated shape. Hence, for most purposes except the forming of very large articles, compression molding of thermoplastics is impractical and until another way of handling these materials was developed they were unsuitable for mass production molding operations and were not widely used therein. The evolution of injection molding has changed this situation radically.

Preparation of Molding Compounds. For custom molding operations, thermoplastics, like thermosetting materials, are first converted into molding powders by the plastics manufacturer before they can be fed into the press of the custom molder. The particular way in which a thermoplastic is made into a molding powder varies with its chemical nature. The older materials all required addition of plasticizers in order to flow satisfactorily on molding. Addition of plasticizers not only serves to make thermoplastics more amenable to mechanical manipulation, but it also toughens them and frequently imparts other desirable characteristics such as water-resistance and non-flammability. A plasticizer is essentially a high-boiling, non-volatile organic compound of relatively low molecular weight which can be admixed with a thermoplastic to improve one or more physical properties. While the majority of plasticizers used today are liquids, a few like camphor, some of the "Aroclors" or chlorinated biphenyls, and diphenyl phthalate are solids. Although a vast amount of work has been done in an effort to systematize our knowledge of plasticizers, no very clear relationships have as yet been shown between their chemical nature and their plasticizing effect. In selecting a plasticizer, it is often necessary to know the particular set of conditions to which the

finished object will be subjected. By adjusting the chemical nature of the plasticizer and the amount employed, the softening point of a given thermoplastic, its flow characteristics, and other properties can be varied throughout a wide range. Dibutyl phthalate, camphor, and triphenyl- and tricresyl-phosphates are common plasticizers, although they are not universally applicable by any manner of means and numerous other compounds, some of which will be mentioned later, are also employed.

Some of the most widely used thermoplastic molding compounds are based on cellulose acetate. Cellulose acetate butyrate has been received with much favor also, while ethyl cellulose is another important member of the family of cellulose plastics. All three of these resins are combined with from 10 to 30 per cent of plasticizer for molding purposes. Once the resin itself is manufactured by chemical conversion of cellulose, it is admixed with a suitable plasticizer in the desired amount and kneaded until homogeneous. While dry mixing can often be employed, the operation may sometimes be facilitated in order to insure homogeneity of the product and to avoid overloading of the kneading machine by addition of a limited amount of volatile solvent so that a heavy dough is formed. Acetone is employed in many cases. Once the materials are well mixed, they are strained by forcing through a wire sieve under pressures of a thousand pounds per square inch or more, in order to remove dirt particles. The strained product is aged in the case of the acetate and acetate butyrate, and the solvent evaporated, preferably with the aid of vacuum. The plastic mass, containing only plasticizer or, at most, but a small amount of residual solvent, is then further mixed on a mill to assure complete homogeneity. Dyes and pigments, if required, can be added at this stage. The milled product is finally chopped into a molding powder of suitable particle size. In both kneading and milling operations, a slight degree of warming is desirable to facilitate satisfactory mixing of the ingredients.

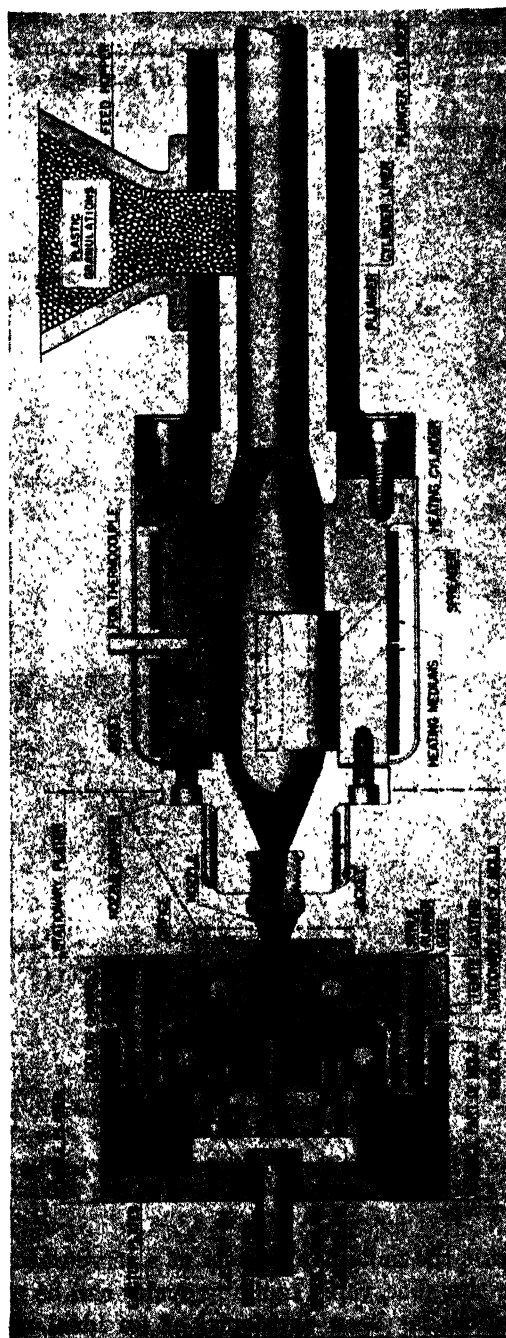
Cellulose derivatives enjoy a large volume of business as thermoplastic molding compounds, but there are also a number of other plastics of recent origin which have rapidly gained favor. Some of them like polyvinylidene chloride, also require the use of plasticizers in order to obtain free-flowing characteristics, but others, notably the methacrylates and polystyrene, may be converted to molding powders by granulation of the plastic material without addition of any plasticizer. In such cases, fillers and coloring materials may, if desired, be mixed with the plastic before grinding or even before polymerization.

Many applications of thermoplastic molding compounds are feasible because of the clarity of these materials. The methacrylates excel in this property. Polystyrene is nearly, although not quite as good, while cellulose acetate and acetate butyrate come third. In the case of these latter

materials, it is customary to add a very small amount of light blue dye to the molding powder so as to neutralize the natural yellow tint of the molded objects. Indeed, it is usually possible to distinguish a transparent cellulosic plastic by the faint blue tinge detectable when it is viewed in depth. Bright colors can be imparted to most thermoplastics by selection of suitable dyes or pigments and, in the case of cellulosic plastics, mottled effects can be obtained by mixing variously colored molding powders of the same plastic, but of different degrees of plasticity.

Injection Molding. Injection molding is the favored method of handling thermoplastic molding compounds. In this operation, molding powder is fed from a hopper into a heating cylinder where it is heated in an annular ring about $\frac{1}{4}$ inch in thickness. Both the cylinder and internal torpedo or spreader are streamlined in order to facilitate flow of the softened plastic out through the nozzle. Heating is carried out by induction, resistance, or circulating fluid. Once raised to the proper temperature for molding, the semi-fluid plastic is forced out of the heating cylinder by means of a plunger, actuated by hydraulic pressure, into the mold which is held against the nozzle by mechanical and hydraulic means. The mold is designed in such a way that the plastic flows first through a sprue, then outward through runners and gates into the cavities. A slug well is provided as an extension of the sprue in order to catch the first shot of plastic remaining in the nozzle of the machine from the previous run. Being somewhat cooler than the main body of ejected plastic, this material might otherwise enter the runners and clog them before the cavities could be filled. The size of the slug well depends upon the design of the rest of the mold and upon the nature of the plastic. Depending upon the size of the article to be molded and the capacity of the machine, the mold may have one or many cavities. The mold is closed before the plastic is injected into it and is provided with means for heating and cooling. When the plastic is run in, it should be at a temperature sufficient to allow passage of the material into all parts of the die, but it must be cooled before opening to such a temperature that the shaped object will not distort upon removal. The pressures used in injection molding are much higher than those required for compression operations, running from 3000 to 30,000 pounds per square inch, although much of this excessive pressure is dissipated by the friction of passage through the cylinder, sprue, runners, and gates before the material enters the cavities. Injection molding temperatures vary with the resin and with its plasticizer content, but generally range from 280 to 440° F. The fundamental principles involved in injection molding are illustrated by Figures 26 to 29.

Several different injection molding machines are manufactured in which mechanical details vary. Their capacity was limited to about an



Courtesy Tennessee Eastman Corp.

Figure 27. Sectional view illustrating general method of injection molding.

ounce when they were first introduced early in the 'thirties, but rapid strides in their development have increased maximum capacity to 36 ounces in some cases, although the maximum of a single cylinder machine

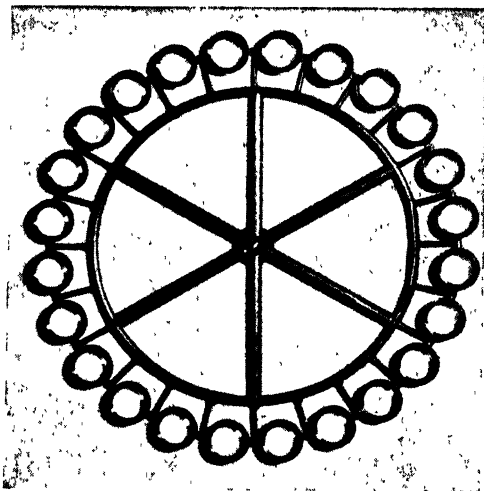
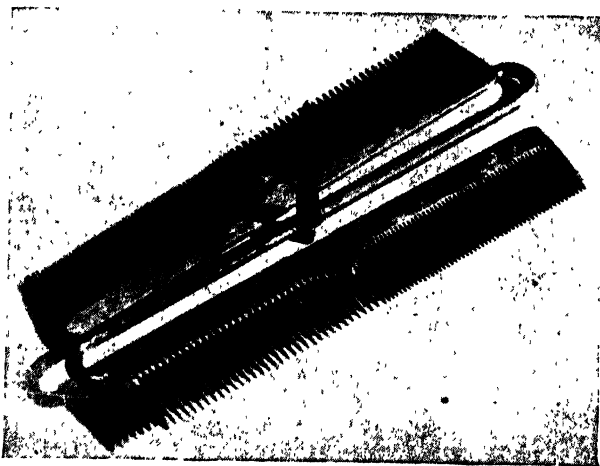


Figure 28a. Glass camera lenses with injection-molded cellulose acetate rims, gates and runners attached.

Courtesy Eric Resistor Corp.

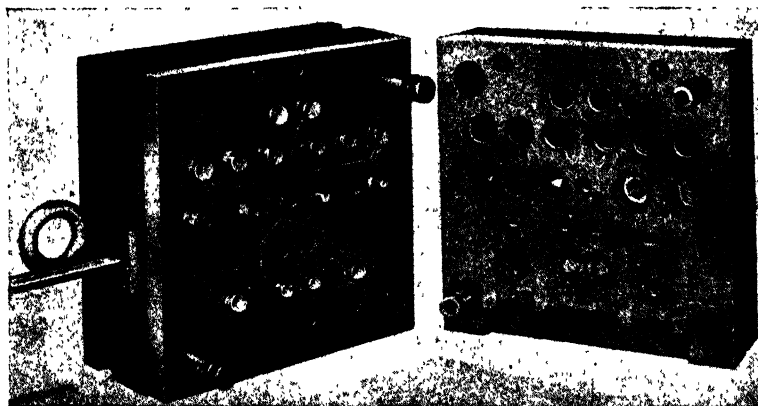
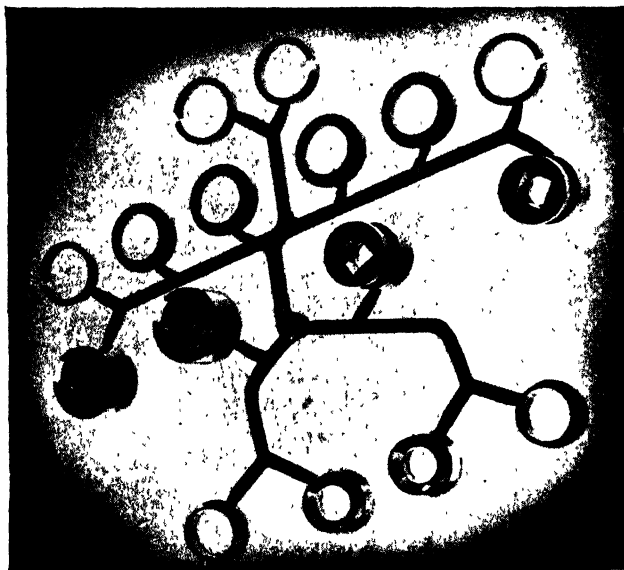


Courtesy General Aniline & Film Corp.

Figure 28b. Injection-molded polyvinylcarbazole combs, runners and sprue attached. Cold slug is visible below sprue.

is 16 ounces. Because the mold can be held at a temperature much below that of the heating chamber, rapid molding cycles can be maintained and this type of operation has been developed as an ideal method of mass

production, especially for small objects where a multiplicity of cavities can be filled with a single shot. Injection molding is well suited to the use of inserts. Even relatively large objects, such as automobile instru-



Courtesy Santay Corp.

Figure 29. Injection-molded fire extinguisher parts with sprue, runners, and gates attached (*above*). Corresponding mold (*below*).

ment panels and glove compartment doors, can be plastic-coated by this means.

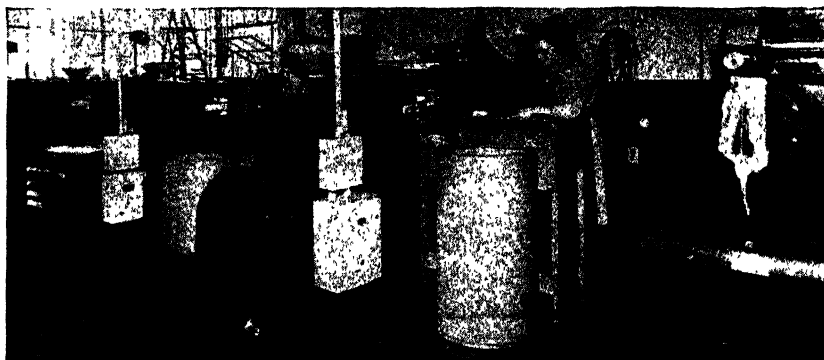
Because the mold is held closed while the plastic is injected into it from the heating cylinder, mold design differs markedly from that used

in compression operations. Injection molds are classified on the basis of the device employed to eject the finished plastic after opening. If pins only are used, it is known as an ejector pin type. If markings left by



Courtesy Monsanto Chemical Co.

Figure 30. Injection molding machine.



Courtesy Boonton Molding Co.

Figure 31. Battery of injection molding presses.

ejector pins cannot be tolerated, an even pressure must be applied across the entire rear surface of the molding by means of a stripper plate, and the mold is known by this name. Loose bar type molds which can be

removed from the injection molding machine and opened manually on the bench are occasionally necessary where the object cannot be removed from the mold by pressure exerted in the direction of travel of the press.

A recent development in the technique of injection molding feeds plastic from a single injection machine into molds retained in several individual compression presses which can be rapidly and consecutively aligned with the nozzle of the heating cylinder.

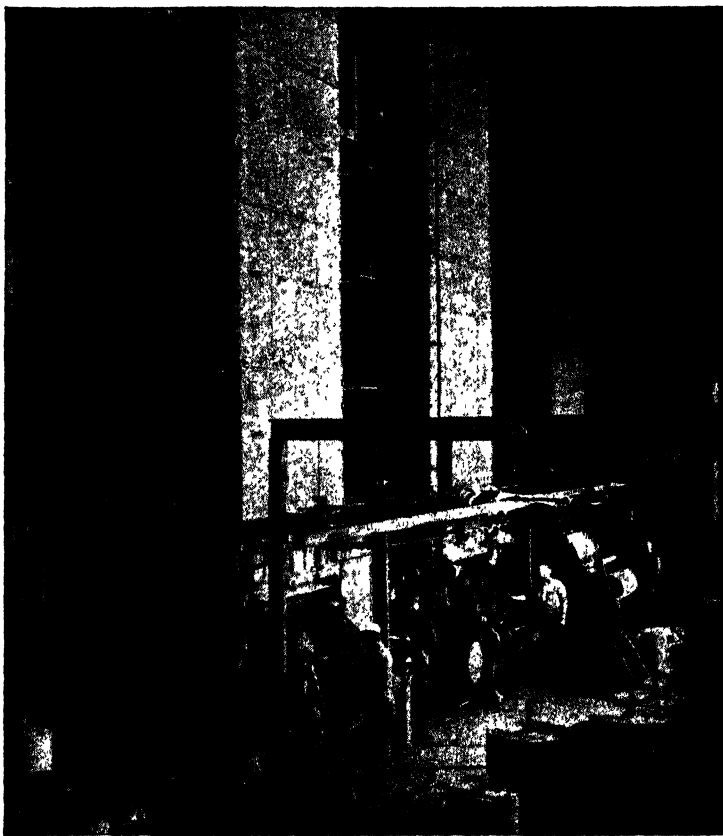
LAMINATED SHAPES

The resistance to shock of many molded plastics leaves much to be desired. For many purposes this may be of relatively little importance, but in other cases, where industrial or architectural applications are involved, it can be a serious factor. By utilizing a filler in the form of a coherent, strong sheet, rather than a powder, it is possible to increase all of the strength characteristics of molded plastics. The use of a lamellar filler, however, places restrictions upon fabricating processes and the shapes obtainable therewith. Sheet, rods, and tubes are the principal forms made of high-pressure laminated plastics. Simple curvatures have been introduced into a limited number of large articles such as refrigerator door panels and serving trays. Standard sizes of phenolic-laminated bearings are also molded by some manufacturers, while, by combination of chopped duck and impregnated fabric, the production of relatively simple molded-laminated pulleys for airplane service has become an important business in recent years. Certain manufacturers produce special shapes, such as channels and angles, in one-piece molds up to seven feet in length. Baseboards, angles, corner nosings, window sills, and decorative trim have been produced from laminated plastics in molds permitting application of pressure from four directions. Such odd shapes, however, represent only a very small portion of the total laminated plastic business.

Phenolics are by far the most common plastics used for laminating purposes. Ureas and melamines are employed to a less extent, particularly in the fabrication of surface sheets for decorative applications. Inasmuch as the purpose of lamination is ordinarily to provide a structurally strong piece, able "to take it," thermoplastics are not often used as a resinous binder, their lack of heat-resistance being an objectionable feature in many applications. This is not always true, however, and there have been a few places where laminated thermoplastics have proved themselves especially suited to the job. Outstanding have been shrapnel-proof breast-plates for A.R.P. suits and wood-veneer laminates for decorative uses.

In the manufacture of laminated plastics, the first step is impregnation of the sheet filler. For this purpose, the paper or cloth is wound up on a roll and passed through a resin solution of carefully controlled concentra-

tion. The sheet may subsequently be allowed to drain or the resin may be scraped from the surface by a doctor knife. In some cases, the plastic solution is applied by means of rollers. In any event, the impregnated sheet is then passed through a drier, either vertical or horizontal, and the solvent evaporated. Depending upon the ratio of resin to filler desired,



Courtesy Westinghouse Electric & Mfg. Co.

Figure 32. Vertical treating towers for impregnating and drying cloth in manufacture of phenolic laminates.

the impregnated sheet may then be given another, or even a third similar treatment. As the impregnated sheet comes out from the drier, it is wound up on a roll at the exit side. For phenolic laminated material, alcohol is the customary solvent. It is added to the resin in the kettle immediately after resinification and vacuum removal of water.

The resin concentration is carefully controlled in order to maintain uniform impregnation conditions. Other factors of importance include the

rate of impregnation and uniformity of thickness of filler. Any unevenness in thickness may result in spots of unimpregnated filler which will weaken the finished structure and alter its mechanical, chemical, and electrical properties.

The dried impregnated material is then cut into sheets for laminating or rolled around mandrels for the production of rods or tubes. The filler and impregnating solution are so carefully balanced that it is possible to



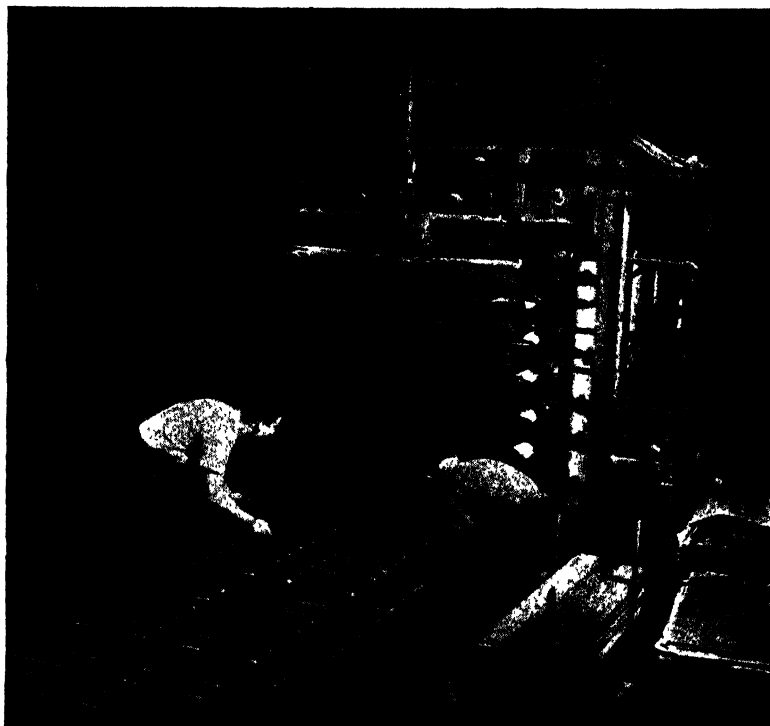
Courtesy Westinghouse Electric & Mfg. Co.

Figure 33. Horizontal impregnating machine used in manufacture of phenolic laminates. The cloth is subsequently dried by infra-red.

weigh out a given quantity of sheets, cut to standard size, and be certain that the finished laminated product will possess a given thickness within slight tolerance limits. The sheets are superimposed upon each other and transferred to a laminating press, usually provided with many heated platens so that a large number of laminates can be made at a single time. Molding is carried out between polished steel plates, using pressures in the order of 1000 to 3000 pounds per square inch and temperatures of 275 to 350° F.

Laminated sheet is made up to 10 inches or more in thickness. Sheets vary in size, depending upon the area of the press platens. They are usually at least 36 inches square. Because of the large bulk of plastic and its poor thermal conductivity characteristics, it requires a much longer

time to cure laminated plastics than to compression mold a powder. With a molding pressure of about 1000 pounds per square inch and a temperature of about 330° F, it is necessary to allow one hour in the press for every inch of thickness of the finished sheet. In addition to this, the pressure must not be released until the platens have been cooled and the body of plastic has been brought to a temperature sufficiently low that



Courtesy Westinghouse Electric & Mfg. Co.

Figure 31. Hydraulic press used in the manufacture of phenolic laminates.

it will not blow or blister upon release of pressure. This precaution does not have to be observed in compression molding powders and it adds considerably to the expense of laminates. It may take from 25 to 30 minutes to heat a sheet $\frac{1}{2}$ inch thick to molding temperature. It will then require approximately $\frac{1}{2}$ hour to cure it. Finally, from 25 to 30 minutes are needed to cool it to such a point that it can be removed safely. The total cycle for a laminate of this thickness is thus about $1\frac{1}{2}$ hours.

The sheet material used as filler in the manufacture of laminated plastics may be any grade of paper, cloth, or other textile, as well as wood

veneer. The most common materials are kraft paper, cotton fabrics—both fine weave and heavy—wood veneer for so-called compregnated wood or “Compreg,” asbestos paper, and asbestos fabric, the last sometimes reinforced with metal wire. For special applications, rayon and glass fiber fabric may be used. Although “Fiberglas” is an expensive base, it imparts exceptional strength characteristics to laminates produced therefrom.



Courtesy Westinghouse Electric & Mfg. Co.

Figure 35. Rolling impregnated cloth into tubes in manufacture of phenolic laminates.

High-strength paper of the Mitscherlich type has also been developed as a base for laminated plastics of superior physical characteristics. The nature of the laminated product is at times improved by incorporation of certain powdered fillers, such as graphite for better frictional properties and aluminum oxide for increased hardness. Coloring materials can also be added to the resin solution before impregnating.

In the production of decorative laminates, the top sheet can be printed with any desired design, either plain or in color. When the surface is to

be white or of a pastel shade, a urea or melamine resin may be used in the top sheet. Metallic inlays on or near the surface are likewise feasible.

Post-forming of thermoset laminates to simple shapes is a practice introduced during World War II which is discussed in Chapter 6 under laminated phenolics.

MOLDED LAMINATES

Since the beginning of World War II there has been a great deal of interest in the development of low pressure methods of laminating. It has been found practicable to use phenolics, ureas, and melamines in this manner. Added to these standard types of thermosetting plastics, have been a number of newer thermohardening materials such as allyl esters of dicarboxylic compounds and copolymerizable mixtures of styrene and unsaturated linear alkyds. Some of these resins are cured without the use of any pressure at all. Others are hardened with the application of pressures ranging from 15 to 200 pounds or more per square inch. Sheet material is impregnated with a solution of the resin or with the monomeric or partially polymerized material, according to type. Saturated sheets—usually cloth or glass fabric—are then laid up against simple and inexpensive forms, preferably metal coated, and the resin is cured with little or no pressure, with or without heat, depending upon the nature of the resin and the catalyst employed for polymerization. Shaped laminated articles can thus be built up, largely by hand. There appears to be no limitation as to size of such articles. Strength properties are usually excellent. Other characteristics vary with the nature of the resin and filler. No-pressure, low-pressure molding methods are further discussed in Chapter 19.

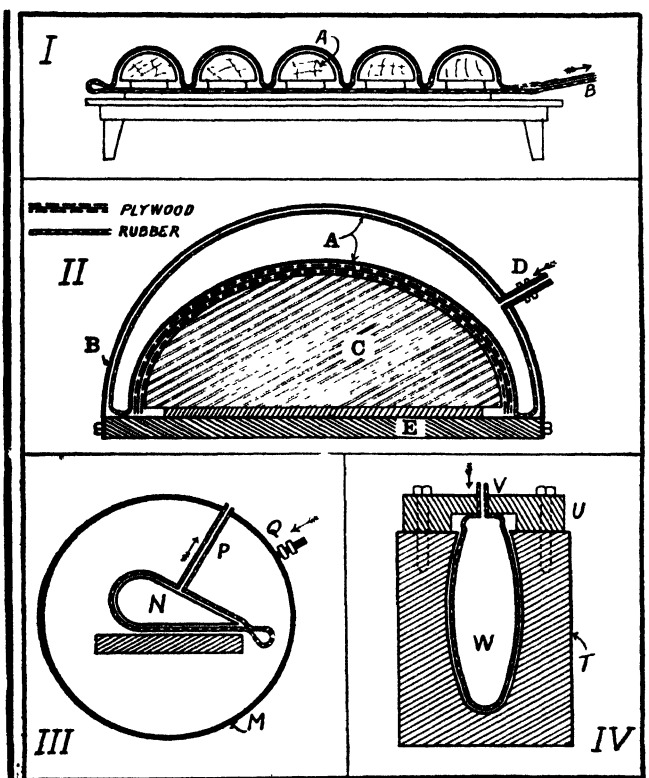
PLYWOOD

Somewhat related to lamination and to no-pressure, low-pressure molding methods are practices used by the manufacturers of resin-bonded plywood. Although wood veneer can be impregnated with resin solution and pressed into Compreg, already mentioned, or into Impreg which is laminated without appreciable compression, much more widely used products are manufactured by the customary techniques of plywood manufacture in which wood veneers are simply bonded together by means of a synthetic resin adhesive. The resin may be applied either from solution or by means of a thin intermediate sheet of impregnated, lightweight tissue paper. Phenolic and urea resins are widely used in the construction of plywood.

Dielectric methods of heating have proved conspicuously successful in bonding and drying plywood.

So-called "bag molding" methods have been evolved for imparting

gentle curvatures to resin-bonded plywood. These processes make use of a simple, inexpensive male or female form against which the wood veneer is laid out. Pressure is then applied to the other side by means



Courtesy The Resinous Products & Chemical Co.

Figure 36. Typical bag-molding methods used in the manufacture of plywood. I. Molding with vacuum bags. A, Solid wood pilasters to be veneer faced. B, Vacuum exhaust outlet. II. Molding a half fuselage. A, Rubber bag inflated through inlet D with air, steam, or hot water. B, Outer steel shell bolted to base E. C, Inside mold (metal with steam pipes or framed wood with slots for rings and longerons. III. Molding of sub-assembly parts. M, Outer steel tank. N, Sub-assembly inside bag. P, Vent (to air or vacuum). Q, Pressure connection for steam. IV. Molding with internal bag. T, Outside mold (metal or heavy wood frame). U, Cap. V, Inlet (air, steam, or hot water). W, Inner rubber bag.

of a rubber bag which may be forced into position by air pressure, suction, or hydraulic pressure. The entire assembly is then heated, usually by placing inside an oven or autoclave, and baked until cured. Bag molding methods are illustrated in Figure 36.

CAST OBJECTS

Most of the molding operations thus far described require simultaneous application of heat and pressure. It is, however, possible to form some plastics by casting in relatively inexpensive molds, curing them without the use of pressure by allowing them to stand at room temperature or slightly above.

The most widely used cast plastics are the methacrylates and phenolics. Various low-pressure, no-pressure resins are also gaining in significance,



Courtesy Catalin Corp.

Figure 37. Pouring casting phenolic resin into lead molds.

while a few other plastics such as polystyrene and furfural resins are cast in very limited amounts.

Phenolics are cast by hand pouring the specially prepared, partially resinified mass into a mold and allowing it to stand for 2 to 12 days, depending upon the temperature and catalyst used. With large castings, longer curing times are required. Two-thirds of the cast phenolics produced in this country are made with the use of lead alloy molds, customarily lead-antimony. Occasionally lead-tin alloys containing up to 7 per cent tin may be employed. Molds are made by dipping a steel mandrel into a bath of molten alloy. After dipping, the mandrel is with-

drawn, the surface layer of lead allowed to harden, and the latter is then stripped from the slightly tapered steel core. After casting, the plastics are removed from the lead molds by means of air hammers. The molds can be remelted and used over. For more complicated designs, split molds are produced with die-casting machines, the halves being provided with interlocking joints so that a fluid-tight container is formed upon assembly. Undercuts can be produced in cast phenolics by this means.



Courtesy Catalin Corp

Figure 38. Steel dipping arbor for producing plate castings of phenolic resins. Lead mold partially removed.

In producing cast objects of approximately 15 cubic inches over-all volume, or greater, it is possible to utilize cores, thus making practicable the production of semi-spherical objects and large hollow shapes. Solid cores are most common, but collapsible rubber cores which can be inflated during use are also employed. Undercut hollow interiors can thus be formed from which the deflated bag can subsequently be removed. Another method of making hollow cast objects is by slushing. In this operation, the mold is filled only partially with resin and is rotated in several planes during cure so that the resin will harden on the sides of the mold. In this

case, as well as when quick resinification is desired to meet production schedules, catalysts are added to the phenolic resin to hurry the setting. In such instances, however, color is usually affected and the inherent brilliance of cast phenolics must be sacrificed.

While lead molds are customarily used for cast phenolics, other materials are also utilized. Glass molds can be employed and broken away from the finished object. Rubber molds, made by depositing a rubber coating from latex upon a plaster of Paris mold, have met with much success in forming objets d'art possessing undercuts and other complicated shapes. Huge statues as much as 9½ feet high have been produced from cast phenolics by the use of such molds.

Cast phenolics must usually be machined and polished after forming. They work easily, so much so in fact that they have met with great favor in home craftsman sets. Because of their easy machinability, it is often cheaper to manufacture small quantities of articles by machining from standard sheet, rod or tube stock. This practice is followed especially in making ladies' costume jewelry, a field in which cast phenolics have excelled because of their clarity and brilliance made possible by the relatively low temperatures used in curing (usually 175° F or lower).

Both sheet and rod are stocked by cast phenolic manufacturers, the latter being available in round, square, triangular, hexagonal, and octagonal forms, as well as more intricate designs such as scalloped, three-leaf clover, and four-leaf clover. Cylinders are also available, as well as polished sheets cast between glass plates and spheres cast within hollow glass balls. Cast phenolics tend to soften slightly at elevated temperatures, so that stock shapes can often be given a desirable curvature by immersing in hot water at 180° F and forming in a wooden jig.

Cast thermoplastics like the methacrylates are made by mechanical processes rather different from those just described for the phenolics. A substantial reduction in volume, often as much as 20 per cent, may occur during polymerization of these materials. Special methods, therefore, must be adopted to discount shrinkage in advance. Commercial methods of casting methacrylates are described in Chapter 18. Cast rods, tubes, and sheets of these resins are available from the resin manufacturers themselves. The clarity of these products exceeds that of molded articles made from molding powders of the same materials. Because of their thermoplasticity, these standard shapes can be bent or formed by gentle heating, a fact of extreme importance in the fabrication of transparent aircraft enclosures.

Botanical and entomological specimens can be embedded in cast methacrylates by partially polymerizing the monomeric material to a syrup before insertion of the specimen. Polymerization may then be

completed under elevated temperature in an autoclave. Polymerization of monomeric material may be carried out at room temperature under atmospheric pressure by building up consecutive layers not more than $\frac{1}{4}$ inch in thickness. This process, however, is very slow and involves considerable risk of contamination.

Slush molding is occasionally applied to thermoplastics reduced to a paste by admixture with a small amount of solvent which can be removed by heat or vacuum during the process.

EXTRUDED SHAPES

For years the metal-working industry has practiced the extrusion of brass, aluminum, and allied products. The rubber industry has likewise perfected its own technique for extrusion of tubing and numerous other endless shapes. In 1890 the first machines were built for continuous extrusion of cellulose nitrate plastics. These machines utilized a wet process which is still practiced by several large concerns which fabricate rods, tubes, bars, and other continuous lengths of cellulose plastics in this way. Within the past decade, however, continuous extrusion of thermoplastics has been greatly expanded by perfection of methods of handling dry powders.

Both wet and dry processes utilize the same fundamental principles of softening the plastic by heat and feeding it at a uniform and carefully controlled rate through a die from which it emerges in a softened state which requires hardening, sometimes by a forced draft or water, before it is cut into standard lengths or wound up on spools, depending upon the shape. Feeding of the plastic to the die is usually accomplished by a worm feed, much as in a meat chopper. Occasionally other feeding means are adopted, especially in the older "stuffing" machines used in some wet extrusion processes.

For wet extrusion, plastic, plasticizer, and solvent are mixed in appropriate kneading machines, or on mills, the process being usually repeated on hot rolls to reduce the final solvent content to the desired point before rolled sheets or chopped pieces are fed into the extruder.

In dry extrusion, the molding powder, usually an especially plasticized grade for extrusion, is fed from a hopper at a uniform rate into the feed cylinder from which it passes into the heating cylinder and finally out through the die. The die is heated and is maintained at a higher temperature than the other parts of the equipment. Inasmuch as this process utilizes solvent-free molding powder, it is especially important that the latter be free from moisture and special drying operations are usually conducted prior to extrusion. Small amounts of moisture give rise to surface blisters and lack of lustre.

Inasmuch as thermoplastics are still fairly soft when they leave the die, the take-off belt may stretch them somewhat as it conveys them away from the machine. This sometimes results in formation of a finished article somewhat smaller than the die orifice and, at times, of different shape. Fortunately extrusion die costs are not as high as those of other types of molds, hence it is possible to carry on a limited amount of



Courtesy Tennessee Eastman Corp.

Figure 39. "Tenite" is extruded by heat and pressure into continuous lengths. Strips made by this process are used for woven furniture, wall-board molding, linoleum and automobile upholstery trim.

experimentation to perfect the shape required to yield a given extruded form.

Extruded plastics must often be seasoned before they attain their final, stable form. This is especially true of products made by the wet process. In the manufacture of tubing to close tolerances, therefore, as in preparation of stock for fountain pen barrels, extruded, aged tubing, somewhat over-size, is warmed and slipped over a core about which it cools to a standard inside diameter. The outside is then ground by centerless grinding to the required dimensions.

Most of the thermoplastics are now extruded in considerable quantities. Rods, tubes, and fancy trim are commonplace. Some, especially polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate, ethyl cellulose, and polyethylene are extruded over electrical wire as insulating coatings, while such plastics as polyvinyl formal, particularly, are extruded as viscous solutions applied as wire coatings.

Extrusion of thermosetting resins has only recently been done in this country, but it has been carried out abroad, especially in England, since 1936. The equipment is necessarily complex since the molding powder must be softened, extruded through a die, and set before it leaves the machine. Extrusion of both phenolic and urea types, however, has been successfully carried out at the rate of about six inches per minute, duplicator cylinders, curtain roller suspensions, and other objects being manufactured from such extruded stock. Thermosetting plastics can also be extruded in curved shapes, provided the radius of curvature is not less than fifteen times the diameter of the extruded stock.

SHEETS, SHEETING, AND FOIL

Many thermoplastics are available in the form of sheets, sheeting, or foil. The methods which are used to produce these flat shapes vary with the nature of the material. Thick sheets are either molded or cast except for cellulose nitrate and acetate which are formed into sheets by cutting off slabs from the mixed material as it comes from the malaxating rolls, stacking, and pressing. Thin sheets of nitrate, acetate, and certain other plastics like some of the vinyls are cut from thick blocks by slicing machines equipped with a blade capable of accurate adjustment and held at an angle to the plane of the table. The latter travels toward the knife. Sheets of very close tolerances are obtainable. Standard cellulose nitrate sheets are 20×50 inches and are available in thicknesses down to 0.003 inch.

Continuous sheets of thermoplastics are produced by extrusion of solutions or doughs through long, slotted openings. Films are made by casting resin solutions upon highly polished endless belts or rotating drums from which the solvent is either evaporated by heat or upon which the sheet material is precipitated by passage through an appropriate bath, as in the case of cellophane. The films are subsequently stripped from their support and wound up into rolls.

Still another method employed for certain types of thermoplastics, especially some of the vinyls and polyethylene, is calendering on rolls much the same as is done in the manufacture of rubber sheeting. This operation is confined to flexible sheeting for which it has been developed with great success.

SWAGED, BLOWN, DIE-PRESSED AND BLANKED ARTICLES

The operation of swaging, otherwise known as swedging or forming, has been applied for years in the fabrication of articles from cellulose nitrate. More recently it has been adapted to other thermoplastics, notably the methacrylates. It is of utmost importance in the manufacture of shaped aircraft enclosures made from acrylics and cellulose acetate. In principle it is very simple, for it involves softening a sheet of thermoplastic material by suitable application of heat, then shaping it over a form and allowing it to cool until rigid. The thermoplastic sheet material may be softened by immersion in a liquid—hot water, glycerol, glycerol-water mixture, or oil, or it may be heated in an oven or, at times, on a hot plate. When it has attained a sufficiently high temperature to permit working, it is pulled over a wood, metal, or plaster of Paris form and held until cool enough to remove without losing its shape. Fitting over the form may be done either manually or mechanically by the use of male and female forms or by hydraulic pressure exerted by a heated fluid against the side of the sheet opposite the form. Acrylates are swaged at temperatures between 220 and 400° F and, in order to prevent marring of the plastic surface, forms for acrylates should be covered with outing flannel, billiard felt, or some other soft material. Marring occurs most readily at higher temperatures, because of the greater softness of the plastic. Dust is also more likely to be caught by the softer surface of a heated methacrylate. The best swaging temperatures for methacrylates lie between 250° and 300° F. Higher temperatures, however, are required for compound curves and deep draws which involve considerable stretching.

Solid sheets of certain thermoplastics, especially cellulose nitrate, are shaped into complicated and intricate forms by blanking. This operation is analogous to punching, but is capable of considerable variation, especially with heated sheets of plastic. In die-pressing, strips or other shapes of solid thermoplastics are cut from sheet material, then pressed into whatever form may be desired by means of a metal mold which can usually be made from relatively soft metals, such as brass or bronze. The blank which is die-pressed should approximate in size and shape the finished object. This is a favorite method for manufacturing combs, toothbrush handles, and other toilet articles made from cellulose nitrate. The die which is employed may be of such construction as to permit overflow of flash, or the blank may be cut so as to allow no excess and the mold thus closed tight. Blanking and die-pressing, although employed with several thermoplastics, are particularly important operations in fabricating nitrocellulose, because this material would seriously decompose

during ordinary injection or compression molding operations. Hence, all nitrate articles are formed from sheet, rod, or tube stock.

Blowing is a process used in fabricating such articles as plastic vials, hollow toys, and Christmas tree ornaments. Two sheets of thermoplastic material are clamped together between halves of a mold and hot compressed air or steam is blown in between them by means of a small nozzle or needle. The mold is preheated before application of air pressure. The



Courtesy Plax Corp.

Figure 40. Side view of machine for extruding and blowing plastic material.

sheets are thus blown out to conform to the shape of the mold and, at the same time, are bonded together around the edge by the pressure of the two halves of the mold applied to the hot, softened material. The mold is, of course, chilled before removal of the object. Blowing operations are usually carried out with molds provided with many cavities. Combinations of swaging and blowing are sometimes employed for the fabrication of intricate shapes. When seams are undesirable in the finished article, tube stock with one end capped or sealed can be blown.

Although differing in the final forms produced and in the methods used to obtain them, all of these operations—swaging, blanking, die-pressing, and blowing—have in common the fact that sheet stock is changed in



Courtesy Plax Corp.

Figure 41. Rear view of machine shown in Figure 40.

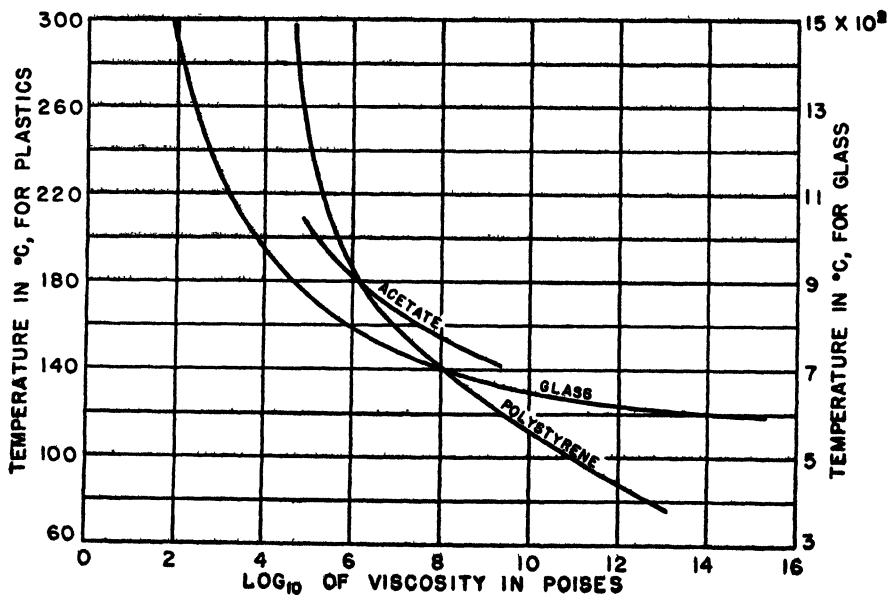


Figure 42. Viscosity-temperature curves for cellulose acetate and polystyrene compared with glass. These plastics are worked at viscosities about 500 times those of glass, illustrating the necessity for using pressure in handling them. Once the parison is formed, both plastics and glass can be blown under comparable air pressures. (Bailey¹⁴)

shape by various devices after it has first been preheated. A significant new development departs somewhat from this general principle in that, by combination of injection molding and blowing methods, such hollow objects as bottles can be produced.

SPUN FILAMENTS

Most extrusion operations are conducted with machines capable of utilizing dies which produce either fancy shapes, as for trim, or cylindrical or rod forms. In the latter case, monofilaments as fine as 0.01 inch in diameter are successfully manufactured. A closely allied operation is carried out in the spinning of fine fibers for textile applications. This process is essentially one of extrusion, although the equipment used differs materially from extrusion machines.

In spinning, the plastic is fed into a hopper from which it passes through the spinneret. Three general types of spinning operations are practiced, typified by nylon, cellulose acetate, and viscose rayon. In the case of nylon, the resin is fused carefully to avoid decomposition and the molten material is then forced through a specially designed spinneret. In other cases, such as cellulose acetate, or "Vinyon," the resin is first dissolved in a solvent like acetone. The solution is then fed into the hopper and extruded through the spinneret, the solvent being evaporated on the other side of the spinneret by means of a current of warm air traveling upward as the fiber moves downward. Viscose rayon, on the other hand, is produced by forcing an aqueous cellulose xanthate solution through the spinneret into a coagulating bath which causes chemical reaction, thereby precipitating regenerated cellulose in the form of a fine fiber.

The spinneret, usually made of platinum, is a small nozzle, about the size of a dime, which contains a number of fine holes, ordinarily from two to five thousandths of an inch in diameter. Filaments as fine as silk or as coarse as carpet wool are thus formed and wound up on spools, to be used in the fabrication of thread. Twisting operations, to yield multi-strand threads, washing, and other procedures such as sizing may be carried out immediately after the filaments are spun, or later, according to the type of fiber and the manufacturer.

An extremely important process which is carried out with fibers spun from some of the newer plastics, especially nylon, "Vinyon," and saran, is cold-stretching. The spun filaments, after being wound, are rewound onto a second reel running at a higher speed, thus stretching the fiber to several times its original length. This serves not only to reduce its diameter, but, far more important, it realigns the linear molecules of which the plastic is composed so that they are more or less parallel to each other.

This has the effect of greatly increasing the strength of the filaments in the direction of stretch. A plastic which, in the massive state may have a tensile strength of 8000 to 10,000 pounds per square inch is thus converted into a filament of 60,000 pounds per square inch tensile or more.

Cold-stretching operations can be carried out with larger monofilaments, up to about $\frac{1}{8}$ inch in diameter, but the increase of tensile strength is less, the greater the diameter and becomes nil above this upper limit. Cold-stretched filaments of the plastics mentioned and of some others, like polystyrene, retain their stretch permanently at normal atmospheric temperatures.

SURFACE COATINGS

One of the most important ways in which synthetic resins are utilized is in the formulation of surface coatings. Drying oils and natural resins have been used for centuries in protective coatings and painters have become accustomed to the odor of these substances and to that of their time-honored thinner, turpentine. The paint and varnish industry was therefore quite naturally reluctant to accept newer synthetic and semi-synthetic resins. Entirely new formulations were required and the solvents utilized therein possessed a "chemical" odor to which the trade long objected. During the last quarter of a century, however, there has been a gradual swing towards the use of synthetic resins and these materials are now indispensable in the formulation of lacquers and varnishes for automobiles and refrigerators, quick-drying interior paints and enamels, traffic paints, and numerous other paints useful in both indoor and outdoor applications. Acid- and alkali-proof paints and concrete coatings rely almost entirely upon the plastics industry for their principal ingredients. So great is the change that alkyd resins, used almost exclusively in products of the paint and varnish industry, are now one of the largest-volume plastics manufactured.

The formulation of protective coatings is part science, part art. The fundamental principles involved are simple, but their practice is complex and difficult and requires a background of extensive experience as well as book-knowledge. In essence, the formulation of a protective coating involves the preparation of a solution of a resinous material which, upon drying, will deposit a coherent, tenacious film of protective material that will prevent corrosion and erosion of the material beneath. Both thermosetting and thermoplastic materials are used in surface coatings. Plasticizers are often added in the formulation of coating materials in order to impart necessary flexibility. In tin can linings, for example, it is essential to have not only a protective layer which adheres well to the base metal, but it must be capable of being crimped during fabrication of the can

without breaking the film. Coloring matter, either dyes or pigments, is necessary in many of these products, while satisfactory formulation must also take into account the spraying or brushing qualities of the solvent, the tendency of the solvent to pick up moisture during evaporation, thus giving rise to "blushing," the deposition of a continuous layer of resinous material from the solvent combination chosen, the ability of the solvent to dissolve a sufficiently high concentration of resin to yield a satisfactory film, and the molecular weight of the resinous base material which, to some extent, determines the viscosity and hence the brushability or sprayability of the coating material. Orange peel effects and other blemishes must be avoided. Plasticizers cannot be used if their volatility is so great that they will evaporate from the film. Many other problems face the formulator of surface coating materials.

Surface coatings may be applied by any of the conventional methods of dipping, brushing, spraying, roller coating, or application by means of a doctor blade.

The development of aqueous emulsions of synthetic resins for coating applications represents a new departure of great significance because it allows the use of the cheapest thinner of all—water.

Flame Spraying

Another method of coating miscellaneous surfaces with synthetic resins of certain special types has been evolved in flame spraying by an adaptation of the Schoop or Schori metallizing gun. Powder is fed to the gun and flame-sprayed onto the surface in question. This process is necessarily restricted to a very few types of unplasticized, heat-stable thermoplastics. It has been used with success for "Thiokol," polyethylene, and some of the vinyls. It is further discussed and illustrated in Chapter 20 under thioplasts.

RESIN-TREATED FABRICS AND PAPER

Closely allied to protective coatings are coated fabrics. The latter, however, may be made not only by coating from solution, but also from emulsion or by means of pastes or calendered material, as in the case of rubber- and synthetic rubber-proofed goods. Dipping, doctoring, and calendering are the principle processes employed in fabric coating.

Numerous resins are also used in treating fabrics to improve their hand and to enhance other properties of the goods. Such applications will be mentioned at various points in later chapters.

Allied to textile treating applications are numerous uses of plastics in coating and impregnating paper to improve physical properties or to impart valuable surface effects.

ADHESIVES

It was formerly said that anybody could make a glue. This rather derogatory axiom is no longer true, for very few can make a good glue, as adhesives formulated from synthetic resins in recent years have amply shown. Both dry and liquid glues are available based upon many different types of synthetic resins. In some cases, dry glues are applied by fusion. In other instances, as with urea-formaldehyde glues, they require addition of a solvent—water in this case. Liquid adhesives may be either 100 per cent liquid resins or resin intermediates which gradually harden, or they may be solutions of one or more resinous materials. Still other adhesive masses are prepared for coating on fabric or sheet material, as in the familiar surgical, industrial, and cellophane tapes. Synthetic resins are also used as bonding agents for abrasive wheels, electric light bulb bases, and water-resistant plywood. For a comprehensive discussion of resin adhesives, see John Delmonte, "Chemistry and Technology of Adhesives," New York, Reinhold Publishing Corp. In press.

A specialized technique utilized in bonding thermoplastic sheeting without the use of an adhesive is known as heat-sealing. This operation may be carried out by any appropriate means of heating the areas to be jointed and then pressing them lightly together. Of particular interest are electronic methods of heating which have been adapted to heat-sealing machines so that thermoplastic film and fabric can be sealed rapidly and easily by running the lapped material through these "electronic sewing machines."

MISCELLANEOUS GOODS

There are various miscellaneous applications of synthetic resins and plastics in addition to those just discussed. In cold molding, for example, as well as in the fabrication of floor tile, resinous materials are used as binders for mineral agglomerates and are pressed into shape at room temperature or slightly above, with or without subsequent baking outside of the mold.

Solutions of some resinous materials, such as mineral oil solutions of polymerized isobutylene, are used as lubricants and greases which possess only slight susceptibility to temperature.

Other plastics, such as complex amino and phenolic condensation products of formaldehyde, are used in water purification as "organolites"—organic chemical analogs of the zeolites.

The diversity of applications of synthetic resins is further indicated by their uses as cement additives, printing ink components, and porous casting sealants,

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Chapter 6

Phenolic Plastics

History

The first purely synthetic resins produced industrially were the phenolics, or phenoplasts as they are sometimes called, developed between 1905 and 1914 by Baekeland, Redman, Aylsworth, and their co-workers. During the latter part of the nineteenth century, cursory studies of the reaction between phenols and aldehydes had already been made by several investigators, both American and European, but these men, among them Adolph von Baeyer of indigo fame and our own Arthur Michael, failed to recognize the commercial value of the resinous products which they had obtained. Renewed interest in this work led to the issuance of a number of patents in the United States, Great Britain, and Germany between 1899 and 1905, among which some of the more interesting were granted to Arthur Smith and to A. Luft. While these patents served as helpful guideposts in a new and unexplored terrain, none was of fundamental significance. It remained for Leo H. Baekeland, an American chemist of Belgian birth and education who had already made a name for himself by developing "Velox" photographic paper, to scale the difficult and forbidding barriers of this new land and reach the fertile plains of moldable plastics.

In 1905, Baekeland began work in his private laboratory in Yonkers, New York, to explore the possibilities of developing a shellac substitute from the products of reaction of phenol and formaldehyde. A year later he announced his results at the New York Chemists' Club. He obtained a series of basic patents on phenolic resins, issued from 1909 onwards, among them U. S. Patent No. 942,699 commonly known as the heat and pressure patent which afterwards withstood considerable litigation. Dr. Baekeland, esteemed throughout the world as the founder of the synthetic resin industry, died on February 23, 1944.

Coincidentally with Baekeland's work during the second decade of this century, two other successful ventures were made in the same field. One was by J. W. Aylsworth, chemical consultant for Thomas Edison, whose initial interest lay in a desire to develop new materials for phonograph records. The other was by L. V. Redman and his co-workers, A. J. Weith

and F. P. Brock, who carried out their investigations at the University of Kansas on a Robert Kennedy Duncan Industrial Fellowship established by the Chicago firm of S. Karpen Brothers for the original purpose of making a superior furniture varnish. It may be noted that the Robert Kennedy Duncan Industrial Fellowship System has, since that time, grown into Mellon Institute of Industrial Research in Pittsburgh.

Companies formed to develop the products of these three interests were as follows:

General Bakelite Co.	October 10, 1910
Condensite Co. of America	September 23, 1910
Redmanol Chemical Products Co.	February 20, 1914

The early days of these three concerns were disturbed by considerable patent litigation that led, finally, to their consolidation on March 22, 1922, by formation of the Bakelite Corporation. In 1939 this company became a unit of the Union Carbide and Carbon Corporation and, in 1944, the Plastics Division of the Carbide and Carbon Chemicals Corporation was consolidated therewith.

Table 2. United States Production and Sales of Phenolic Resins, 1944^{a,b}

Material	Production (1,000 lb net resin content ^a)	Sales		
		Quantity (1,000 lb net resin content ^a)	Value (1,000 dollars)	Unit value (per lb)
Coal-tar acid resins, total	197,312	188,361	52,659	0.28
Phenolic resins, total	158,944	153,365	42,458	0.28
<i>p</i> -ter-alkylphenol-aldehyde	2,573	2,511	806	0.32
cresol-formaldehyde, total	14,825	15,135	3,546	0.23
for laminating	12,481	12,796	2,889	0.23
for miscellaneous uses	2,344	2,339	657	0.28
phenol-formaldehyde, total	116,203	111,336	33,574	0.30
for molding	42,094	41,868	15,726	0.38
for protective coatings	10,294	10,112	3,792	0.38
for laminating	27,173	23,169	5,527	0.24
for adhesives	21,080	20,787	3,841	0.18
for textile, paper, and leather treatment	318	Combined with miscellaneous uses		
for miscellaneous uses	15,244	15,400	4,688	0.30
phenol-formaldehyde, abietic acid modified	2,020	1,625	237	0.15
phenol-formaldehyde, abietic acid ester modified	20,889	20,627	3,492	0.17
other phenolic resins	2,434	2,131	803	0.38
Mixed phenolic (tar acid), total	38,368	34,996	10,201	0.29
cresylic acid-formaldehyde	6,720	4,147	1,089	0.26
cresols and xylenols-aldehyde	1,740	1,341	385	0.29
other mixed phenolic resins	29,908	29,508	8,727	0.30

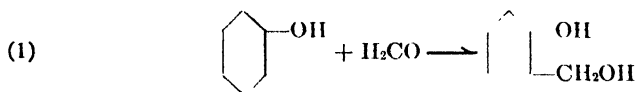
* Data on production and sales are shown in terms of net resin content, i.e., exclusive of all fillers, drying agents, dyes and plasticizers. Chemical modifiers such as abietic acid and special oils are considered part of the net resin content when they are chemically combined with the principal resin.

Upon expiration of the basic patents in 1926, several new producers entered the field of phenolic resins, with consequent competitive price cuts and widening of markets. About thirty companies now make molding and laminating phenolics, either for sale to custom molders, or for their own consumption. Cast phenolics and phenolic coating materials were also introduced at the beginning of the industry. Varnish manufacturers, however, did not accept these early resins generally, so that phenolic coatings were restricted to thin baked-on metal lacquers and were used especially for brass bedsteads. Revised formulations of improved quality are more recent developments of the past fifteen years. Cast phenolics have also come into prominence during the same period.

The distribution of phenolic resins in 1944 according to type and end use has been estimated in Table 2.

Chemistry

If equimolecular amounts of phenol and formaldehyde are reacted together in aqueous solution by long standing at room temperature or below, in the presence of a mild alkaline catalyst, a relatively simple reaction occurs according to the equation:



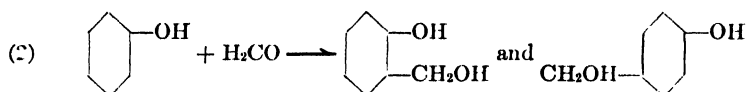
The product, *o*-methylol phenol, has been given the common name, saligenin. Both this compound and its *para* isomer can be obtained by carefully working up the reaction products from an exactly neutralized solution. Upon gentle heating or upon treatment with strong acids, saligenin is converted to a condensation polymer whose molecular weight varies according to conditions. It has been called saliretin. It is a yellowish powder, soluble in both alcohol and alkali and is the anhydride formed by loss of water from 3 to 8 molecules of monomeric saligenin. If reaction conditions—especially the methylene ratio—are not controlled, both saligenin and saliretin are only intermediate, short-lived products in a complicated series of reactions which finally result in tridimensional condensation polymers of high molecular weight, infusible and insoluble in ordinary solvents.

Although infusible, insoluble resins are the invariable end products of drastic reaction between numerous phenolic compounds and aldehydes, the nature of both the intermediates and the final materials obtained under milder conditions can be widely varied by careful control. Several factors influence the course of resinification. Among them the most important are: (1) Acidic or basic nature of the catalyst. (2) Concentra-

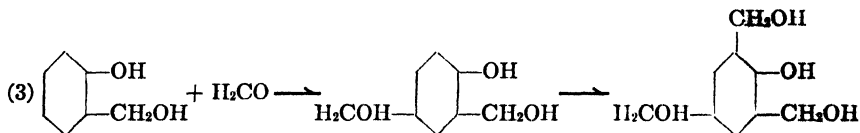
tion of catalyst. (3) Ratio of aldehyde to phenol. (4) Structure of phenol. (5) Structure of aldehyde. (6) Time and temperature of reaction. (7) Presence and nature of modifying agents.

In considering the first three factors, we shall specifically refer only to phenol and formaldehyde, but similar generalizations apply to their homologs and analogs.

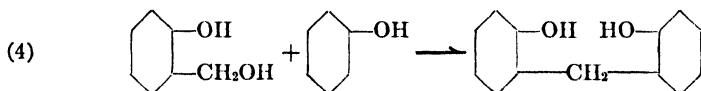
(1) *Acidic or basic nature of the catalyst.* The first reaction occurring in the formation of a phenolic resin is the production of saligenin or its corresponding *para* isomer.



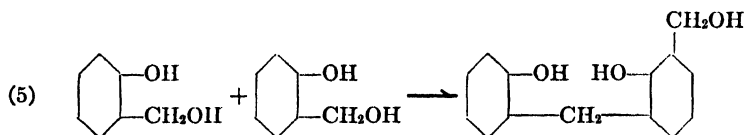
Saligenin may then react with more formaldehyde to form polymethylol phenols,



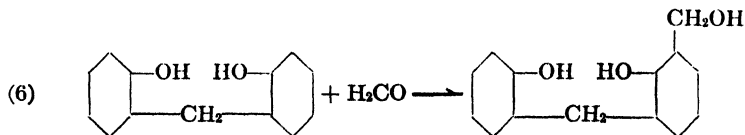
Or it may react with more phenol to yield a dihydroxydiphenylmethane:



Still another reaction which saligenin may undergo is condensation of two molecules to a dihydroxymethyloldiphenylmethane:

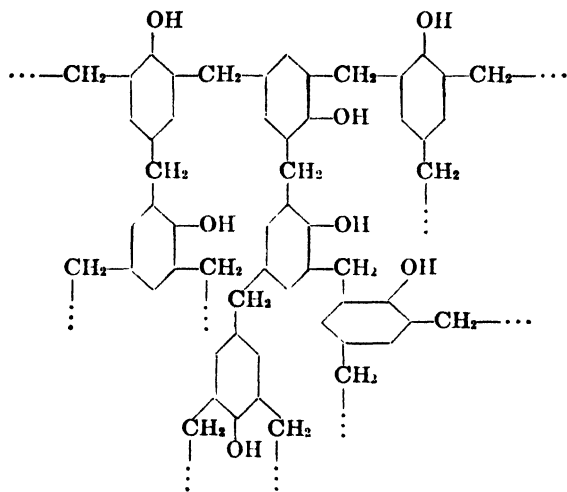


The reaction product of equation (5) can also be obtained by addition of formaldehyde to the product of equation (4):



These are all type reactions which can take place in *para* position as well as *ortho* and which are capable of repetition an indefinite number of times to build up large molecules. Among them, types (2), (3), and (4) are the most important.

In the presence of an alkaline catalyst the rates of reactions of types (2) and (3) are much greater than that of type (4). Hence, when alkaline catalysts are employed with a sufficient quantity of formaldehyde, polymethylolphenols are formed in appreciable amounts before reaction of type (4) sets in. Tridimensional structures are therefore built up when these polymethylolphenols subsequently react in the sense of equations (4) and (5), and a complex product is obtained which might be represented in part as follows:



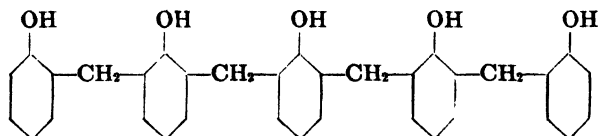
When the structure becomes sufficiently large, such tridimensional polymers are insoluble and infusible.

The formation of condensation products between phenol and formaldehyde by alkaline catalysis proceeds gradually, the resin becoming more complex as its molecular weight and netting index increase. According to Baekeland's early observations, which have been generally accepted since then, there are three more or less distinct stages which are reached during resinification, and these stages are characterized both by the appearance of the resin and by its solubility. They are known as A, B, and C. The A-stage resin is a low molecular weight condensation product obtained during the early period of reaction. It may be liquid, solid, or semi-solid and it is readily soluble in acetone. An A-stage resin is also sometimes called a resol. Upon further heating of A, a B-stage resin forms, known as a resitol. A resitol is usually solid and is insoluble in acetone, although it is swelled thereby. It can be softened by heat a limited number of times or held in the softened state for a limited period before it converts to the C-stage or fully cured plastic, otherwise known as a resite. This final stage is completely insoluble in acetone and infusible. A, B, and

C stage resins correspond to increasing molecular weight and ~~netting~~ index.

It is an important fact that in alkaline catalysis, the condensation can be interrupted at any time by cooling, and continued again by reheating. It is this fact which permits the molding of thermosetting phenolics. In the production of resins for molding powders by the one stage process, alkaline condensation is brought about and the reaction stopped during the B-stage. The resitol thus formed is advanced to the proper degree of plasticity by milling on hot rolls, mixed with filler, coloring matter, and mold lubricant and sold to the trade as molding powder. During molding, this B-stage resitol is converted under heat and pressure to the final C-stage resite.

In the presence of an acid catalyst, the rate of reaction of type (4) is greater than that of types (2) and (3). This leads to formation of linear chains. While many isomeric and branched structures are possible, a typical formula might be as follows:



Because these polymers are linear, they are also thermoplastic. Forced reaction with hot concentrated acid results in such violent condensation that tridimensional structures are built up as well as linear ones, but under properly controlled conditions acid condensation of phenol and formaldehyde leads to linear thermoplastic polymers. These products have received the general term, "novolacs." They are usually brittle, hemicolloidal solids. Some of them are oil-soluble and are widely used in the formulation of paints, lacquers, and varnishes.

It is possible to react a novolac with more formaldehyde under alkaline conditions, in accordance with equation (6). The end product is a thermoset, infusible, and insoluble resite, similar to what would have been obtained finally by direct alkaline reaction. Advantage is taken of this fact in the manufacture of industrial molding powders by the two-stage process, in which novolacs and hexamethylene tetramine are ground or milled together into a molding powder, the hexa supplying both the necessary excess of methylene groups and the basic catalyst required for conversion of the resin to a tridimensional structure. In a certain sense, therefore, such two-stage phenolic resins are not only thermosetting; they are chemosetting as well, because they are cured by reaction with an external chemical, hexamethylene tetramine.

It is also possible to produce A- or early B-stage resins by alkaline

catalysis and then continue resinification with an acid. This results in formation of a B-stage resin free from methylol groups which can be used in molding powders in conjunction with hexamethylene tetramine, but which will not convert to the C-stage upon standing alone at room temperature, as will alkali-catalyzed phenolic resins.

(2) *Concentration of catalyst.* Alkaline catalysis of phenolic resin formation is independent of the hydroxide ion concentration, except where

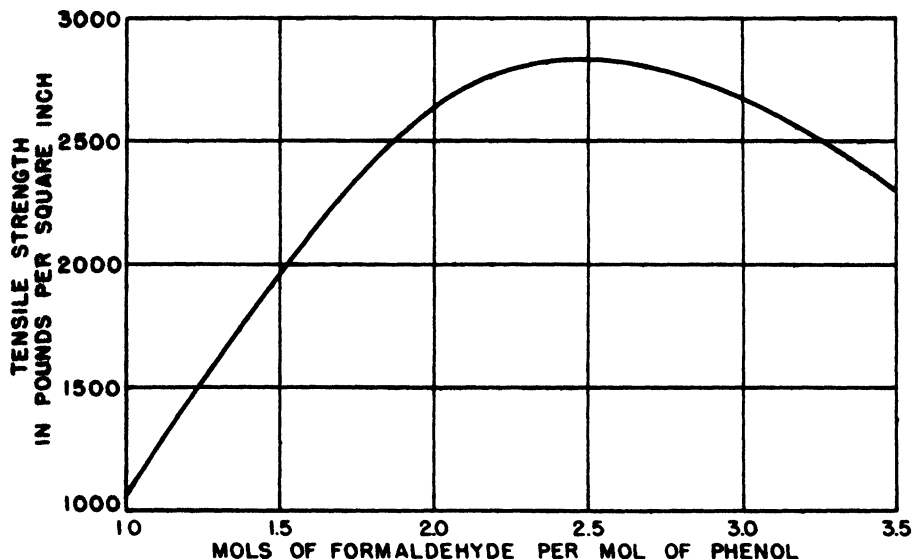


Figure 43. Relation between tensile strength and composition of cast phenolic resins. (Thompson⁷⁹)

the latter is low. At 100°, for example, it has been found that the rate of resinification is practically independent of the amount of sodium hydroxide present between proportions of 5 and 100 mole per cent, based on the phenol. Acid resinification, on the other hand, is very sensitive to concentration of catalyst, the rate being a direct function of hydrogen ion concentration.

(3) *Ratio of aldehyde to phenol.* From the partial structures of tri-dimensional and linear resins given above, it can be seen that while phenol and formaldehyde react in slightly less than equimolar amounts to form acid-condensed thermoplastic polymers, more than one mole of formaldehyde is required per mole of phenol to form a thermosetting resin. In the tridimensional formula shown earlier, the ratio of formaldehyde to phenol is 2:1. This is greater than is ordinarily used industrially in the production of molding and laminating resins, where ratios ranging

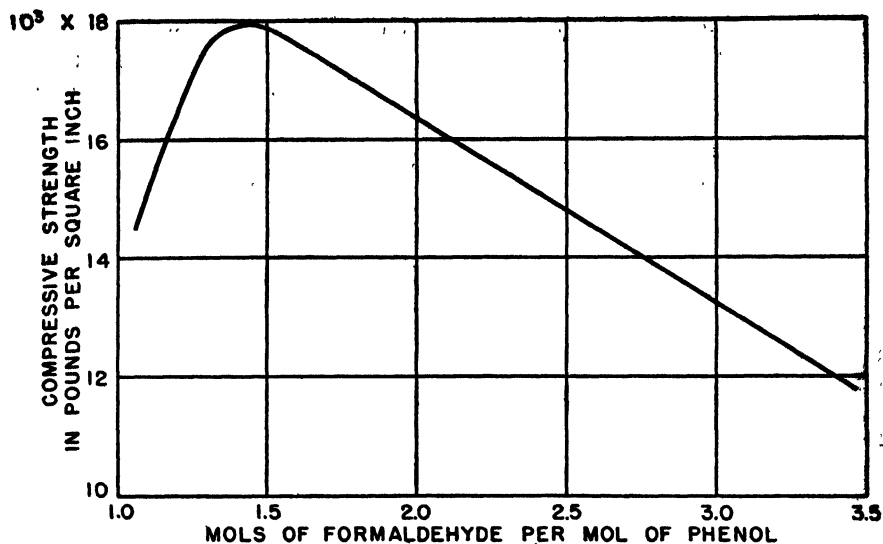


Figure 44. Relation between compressive strength and composition of cast phenolic resins. (Thompson ⁷⁹)

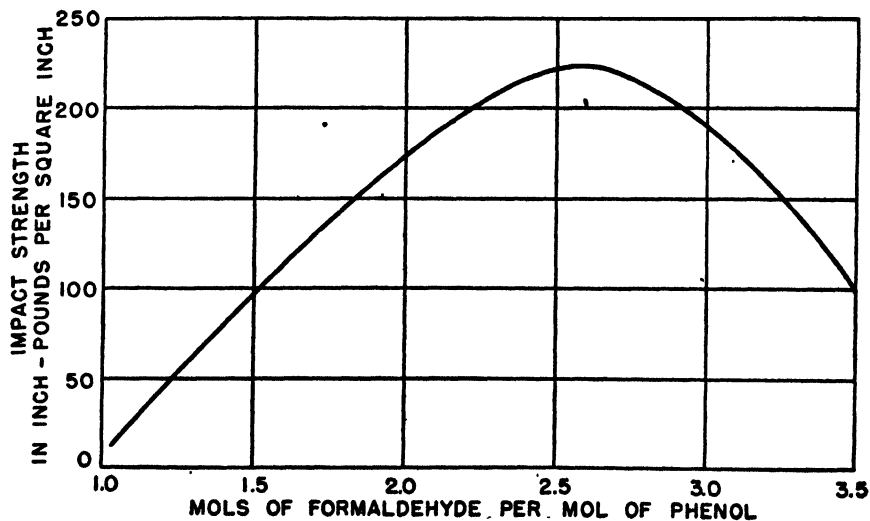


Figure 45. Relation between Izod impact strength and composition of cast phenolic resins. (Thompson ⁷⁹)

from 1.1:1 to 1.5:1 are common practice. In the production of cast phenolics, higher ratios of formaldehyde to phenol may be used. Relationships between this ratio and certain physical properties of such plastics are shown in Figures 43 to 45.

It has already been noted that the formaldehyde need not all be added at one time, a fact of which advantage is taken in the manufacture of molding powders by the two-stage process. In the linear formula shown above, the formaldehyde to phenol ratio is 4:5. The greater this ratio, the shorter is the time required for resinification in the presence of an alkaline catalyst. This is particularly important in determining the amount of hexa to be used in molding powders, for the speed of cure can be widely varied by this means.

(4) *Structure of phenol.* The structure of the phenol exercises a marked influence upon the nature of the resinification product. It determines its ability to form curable resins, as well as the rate of resinification and the solubility of the resins produced.

It is a well known principle of aromatic organic chemistry that a hydroxyl group on the benzene ring orients an entering group *ortho* or *para*. Hence, as indicated by equations (2) to (6), formaldehyde reacts with phenol and its homologs by union at the *ortho* and *para* positions. The number of *ortho* and *para* positions which are open in the phenol, therefore, usually limits the amount of formaldehyde which can be taken up. Highly cured C-stage resins can be obtained only from phenols having all three *ortho* and *para* positions free. Those having but two positions free yield either non-curable resins or products which cure but partially or, at best, very slowly. Low molecular weight products, only, can be obtained from phenols which have but a single open position, while those in which all three *ortho* and *para* positions are blocked do not react with formaldehyde. Phenols may therefore be classified in four different categories, according to the number of open positions which are free to react with formaldehyde, as shown at the top of page 122.

Fully curable resins can be obtained from mixtures of phenols which contain a sufficiently large portion of type 3 compounds. Thus, cresylic acids which have only a 50 per cent *m*-cresol content yield curable products, although it is customary to hold the *o*-cresol as low as possible—usually to less than 5 per cent.

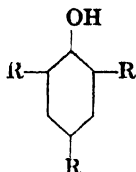
Resins for molding powders are made from pure phenol or from mixtures of tar acids containing chiefly phenol.

Cast resins are made from pure phenol, the synthetic product being used in order to obtain as good color as possible.

Laminating resins were produced largely from cresols and xylenols before World War II. Recently, because of cresol shortages, they have been

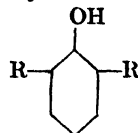
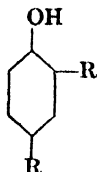
Type 0

No open positions.—Unreactive with formaldehyde.



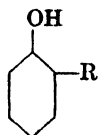
Type 1

One open position.—Low molecular weight condensation products with formaldehyde.



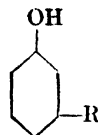
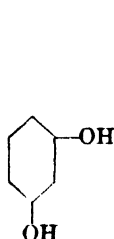
Type 2

Two open positions.—Uncurable, difficultly or partially curable resins with formaldehyde.



Type 3

Three open positions.—Highly curable resins with formaldehyde.



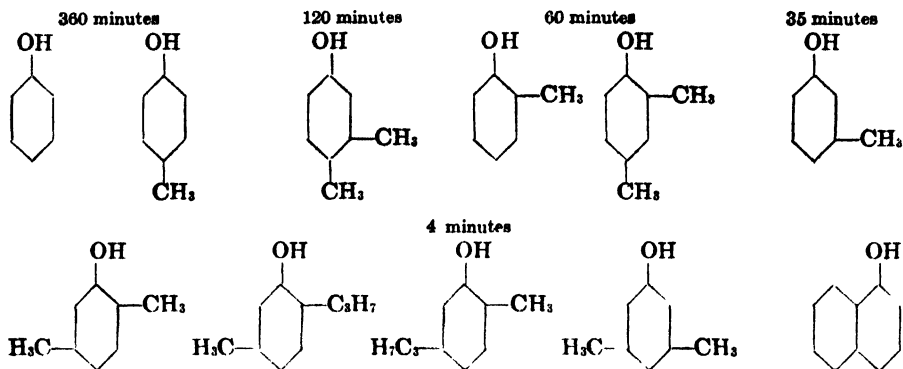
made in considerable quantity from phenol. For coating resins, "natural" (coal tar distillate) homologs of phenol are employed, as well as several synthetic alkylated phenols, especially *p*-ter-butyl phenol, *p*-ter-amyl phenol, *p*-sec-octyl phenol, and *p*-hydroxydiphenyl.

Over the ten-year period, 1933–1943, approximately 66 per cent of all phenolic resins were made from phenol, 17½ per cent from mixtures of phenol and cresol, 10 per cent from cresols and cresylic acid, and 6½ per cent from cresol-xylene mixtures, xylenols, and alkylated phenols. Estimated 1943 consumption of phenol in the manufacture of phenoplasts of all kinds was 56,900 short tons. The corresponding estimate for cresols, cresylic acid, and xylenols was 13,300 tons.

Under acid conditions, the rate of resinification is not greatly affected by the structure of the phenol, but under the influence of alkaline catalysts there is marked variation in velocity from one phenol to another. Granger has determined the time required for an equimolar formaldehyde and sodium phenolate reaction mixture to reach an advanced stage at 100°. Approximately the same degree of resinification was attained in each case, the time required with various phenols being shown on the next page.

Resorcinol is resinified with extreme rapidity.

The structure of the phenol also exercises a marked effect upon the



solubility of the resultant resin. Acetone is a universal solvent for any phenolic resin which is in such a stage of condensation that it can be dissolved at all; this includes both novolacs and A-stage resins. If alkaline condensation is not carried beyond the soluble A-stage, there is relatively little difference in the solubility of alkali and acid catalysed condensation products from the same phenol, but there is considerable variation from one phenol to another. Granger reports the solubilities shown in Tables 3 and 4.

Table 3. Solubility of Novolacs ³⁸

Phenol	Aqueous NaOH	Alcohol	Ether	Ethyl Acetate	Chloroform	Benzene	CCl ₄
<i>p</i> -cresol	Insol.	Insol.	Sol.	Sol.	Sol.	Sol.	Sol.
<i>o</i> -cresol	Sol.	Sol.	Sol.	Sol.	Sol.	Ltd.	Insol.
<i>m</i> -cresol	Sol.	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.
3,5-xylenol	Sol.	Sol.	Sol.	Sol.	Sol.	Ltd.	Insol.
<i>p</i> -phenylphenol	Insol.	Insol.	Ltd.	Ltd.	Sol.	Sol.	Ltd.

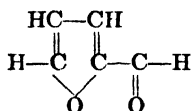
Table 4. Solubility of Alkaline Condensation Products of Phenols and Formaldehyde ³⁸

Phenol	Aqueous NaOH	Alcohol	Ether	Benzene	CCl ₄
phenol	Sol.	Sol.	Insol.	Insol.	Insol.
<i>m</i> -cresol	Sol.	Sol.	Insol.	Insol.	Insol.
<i>o</i> -cresol	Sol.	Sol.	Ltd.	Ltd.	Insol.
<i>p</i> -cresol	Ltd.	Insol.	Ltd.	Sol.	Sol.
2,4-xylenol	Sol.	Sol.	Sol.	Sol.	Sol.
2,5-xylenol	Sol.	Sol.	Sol.	Ltd.	Ltd.
3,4-xylenol	Ltd.	Insol.	Insol.	Sol.	Ltd.
3,5-xylenol	Sol.	Sol.	Sol.	Insol.	Insol.
thymol	Ltd.	Ltd.	Sol.	Sol.	Ltd.
carvacrol	Ltd.	Ltd.	Sol.	Sol.	Sol.
α -naphthol	Sol.	Ltd.	Ltd.	Ltd.	Ltd.
<i>p</i> -phenylphenol	Insol.	Insol.	Ltd.	Sol.	Ltd.

There is also considerable variation in the solubility of phenolic resins in drying oils, depending upon the structure of the phenol. Here again, little influence is exercised by the acidic or basic nature of the catalyst, although the curability of the resin is affected thereby. Among the more

common phenols, phenol itself, *m*- and *o*-cresol, and the naphthols are the only ones yielding resins which are insoluble in drying oils. *Para* substituted phenols yield resins that dissolve especially easily, while 2,4-, 2,5-, 3,4-, and 3,5-xylenols, thymol, and carvacrol give resins which dissolve in tung oil upon heating. The tolerance for petroleum thinners varies, as can be judged from the preceding tables, with *para* substituted phenols outstanding. Resins from *p*-ter-butyl phenol, *p*-ter-amyl phenol, *p*-sec-octyl phenol, and *p*-phenyl phenol yield condensation products which serve as excellent resinous bases for drying oil paints and lacquers.

(5) *Structure of aldehyde.* By far the most important aldehyde for phenolic resins is formaldehyde. While many other aldehydes and ketones give resinous products with phenol, most of them are not suitable for either molding powders or varnishes. Acetone is used to a limited extent, especially in oil-soluble resins. Glyoxal, $\text{HCO}-\text{CHO}$, a newcomer to the ranks of commercially available chemicals, is being developed as a component of phenolic resins. Furfural,



is utilized in the production of those resins sold under the trade-mark "Durite." Resins made from furfural remain in the B-stage at moderately elevated temperatures for somewhat longer periods of time than corresponding formaldehyde materials. During early efforts to adapt injection molding methods to thermosetting plastics, this fact was of some importance for it permitted their use in injection molding equipment without jamming the plasticizing chamber or its orifice. Other phenolics, however, have now been developed for injection molding, a process which, applied to thermosetting plastics in general has come to be known as jet molding.

(6) *Time and temperature of reaction.* These two reaction conditions obviously affect resinification, as in all organic operations. They must be carefully controlled during the manufacture of resins and molding compounds in order to obtain products of uniform characteristics, and they must also be no less accurately controlled during molding to insure complete conversion from B- to C-stage resin under satisfactory conditions of flow without under-cure on the one hand, or without over-cure (burning) on the other.

(7) *Presence and nature of modifying agents.* The nature of phenolic resins can be greatly altered by incorporation of modifying agents in their molecular structure. Modifiers are particularly important in the preparation of phenolic resins for coating applications. Natural resins,

fatty acids, glycerol, and certain synthetic resins, especially alkyds, are common. Extenders, which may or may not be chemically combined with the phenolic resin, have been used to some degree in times of phenol shortages as components of molding powders. Typical extenders are lignin preparations and rosin products like "Vinsol."

Molding Materials

Manufacture. In producing a phenolic resin, a suitably selected phenol or cresylic acid cut is heated together with the proper amount of formalin or paraform if a "wet process" is used, or with hexamethylene tetramine if a "dry process" is employed. In the latter case, hexa supplies its own catalyst—ammonia, but the dry process is relatively expensive and is not commonly employed. In the wet process, either an acidic or basic catalyst is added and the batch is heated to start reaction. Being exothermic, resinification proceeds subsequently without the aid of external heating. When reaction has gone far enough, the batch is cooled, vacuum applied to remove water, and the product poured out of the reactor and further cooled. It is then ready to be admixed with suitable fillers, lubricants, pigments, and, if necessary, hardening agents such as hexa. The resin itself usually corresponds to about 50 per cent of the finished powder. The mixing process is carried out on rolls working against each other at different rates, like those used in the rubber industry. The rolls are heated where necessary in order to advance the resin to such a point that it will possess the desired degree of plasticity. Grinding and batch blending are then utilized in order to assure proper control of particle size and uniformity.

Because of their thermosetting characteristics, phenolics are molded primarily by compression and transfer methods, described in Chapter 5. Jet molding is a promising recent innovation. Continuous extrusion of phenolics has been practiced to some extent in England. Compression molding is carried out at temperatures of 270–360° F under 2000 to 5000 pounds per square inch. Transfer operations are usually conducted under higher pressures. Advantages gained by electronic preheating have been enumerated in the preceding chapter; decrease in curing time effected thereby is shown graphically in Figure 52, page 130.

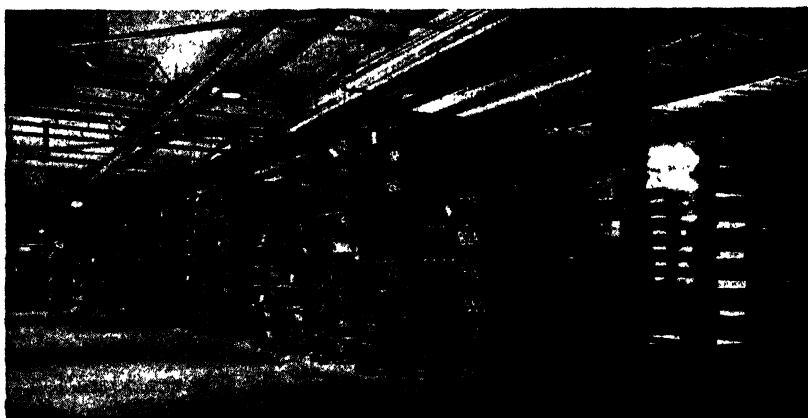
Fillers. Practically all phenolic molding powders contain fillers, used to improve moldability or to enhance various physical properties of the finished plastic. In general purpose molding powders, decrease in cost resulting from the presence of an inexpensive filler is sometimes an important factor, but even then it is by no means the sole consideration.

In recent years there have been developed a very limited number of 100 per cent phenolic resin molding powders which yield transparent



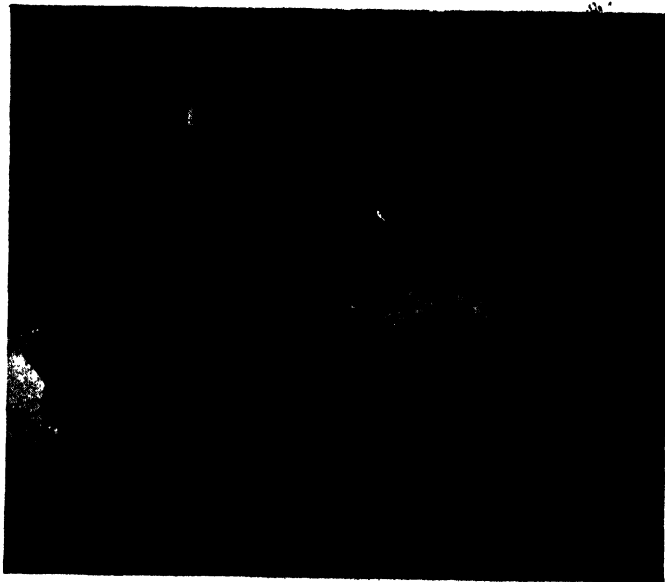
Courtesy Bakelite Corp.

Figure 46. Large phenolic resin still, with weigh tank at top left, shaft in center above still containing agitator which rotates inside still, and condensing unit at right.



Courtesy Bakelite Corp.

Figure 47. Pans of phenolic resin racked up in the cooling and storage area.



Courtesy Bakelite Corp.

Figure 48. Cracking the hardened phenolic resin.



Courtesy Bakelite Corp.

Figure 49. A powdering unit being charged with chips of phenolic resin.

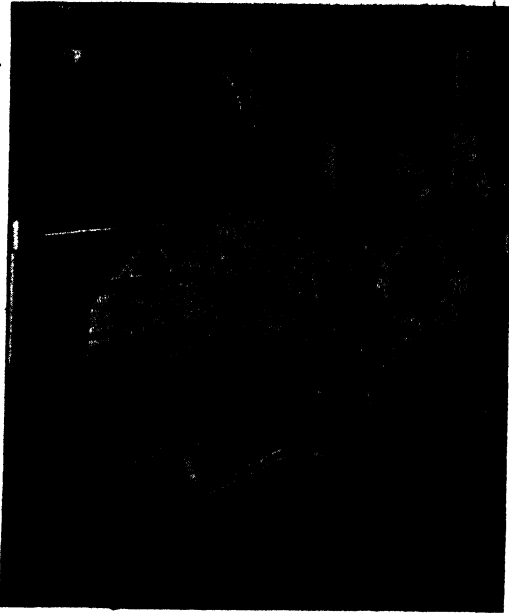


Figure 50. Woodflour or other fillers and coloring materials are mixed with phenolic resins on heated compounding rolls as shown here and the cure is advanced to such a stage that the products will harden rapidly in the mold under application of heat and pressure.

Courtesy Bakelite Corp.



Courtesy Bakelite Corp.

Figure 51. A mixer for high impact material being emptied on conveyor.

articles available in colors ranging from light amber to ruby and green. These materials are difficult to mold and are not in great demand except for those applications where the heat resistance and dimensional stability of a thermosetting resin is required in a transparent plastic as, for example, lenses of the rear lights of automobiles and traffic lights.

The most important fillers are listed below:

Cellulosic

- Wood flour
- Cotton linters
- Walnut shell flour
- Chopped fabric
- Creped paper
- Kraft wood pulp
- Sisal

Mineral

- Clays
- Diatomaceous earth
- Talc
- Slate
- Asbestos powder and fiber
- Mica
- Graphite
- Metal powders (iron and copper)
- Barytes

Miscellaneous

- Carbon black
- Soybean flour and protein

Wood flour, of about 100 mesh average particle size and 50 mesh maximum, is the most common filler and is used for general purpose molding compounds. It is best prepared by attrition grinding (to preserve the fibrous structure of the wood) of selected knot-free and bark-free woods—usually soft woods such as pine, fir, spruce, poplar, basswood, and cottonwood. Wood flour filled resins flow easily in the mold and handle well, yielding articles possessing excellent appearance, with filler uniformly distributed throughout. Good electrical properties, good tensile strength, and low heat conductivity characterize the moldings. Their impact strength, on the other hand, is only fair. Walnut shell flour gives products of decreased water absorption because of its cutin content.

For more severe impact requirements, other fillers are required as shown by Figure 53. Cotton linters yield articles which are better in this respect, while chopped fabric, shredded textiles, and long-fibered wood pulp (kraft) give molded objects of outstanding resistance to shock. Sisal fiber has been developed as a filler for plastics of light weight and high impact re-

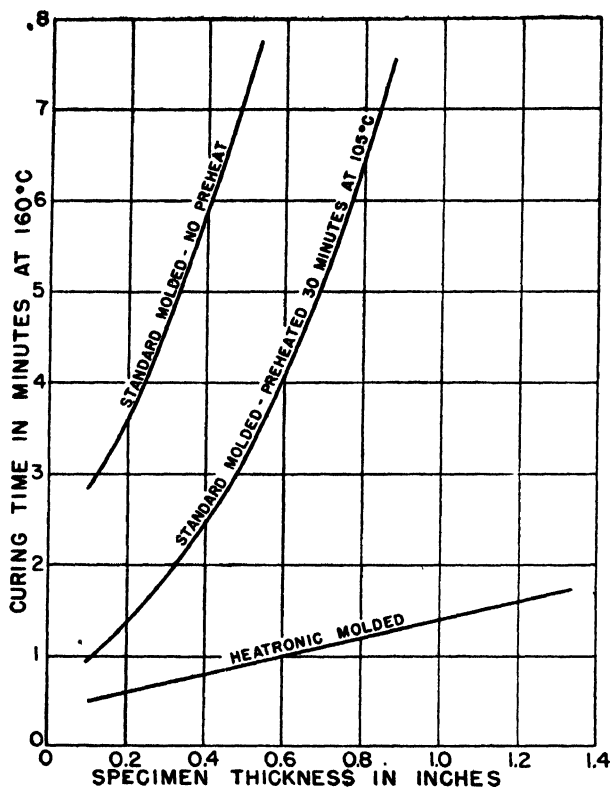


Figure 52. Comparison of thickness *vs.* optimum curing time for specimens of wood flour filled and fabric filled phenolic materials molded without preheat, with oven preheat, and with high frequency preheat. (Meharg⁵¹)

sistance. These fillers, however, increase molding difficulties approximately in the order named. The bulk factor of molding compounds based on all but cotton linters is usually high.

Chopped fabric is impregnated with resin solution, dried free of solvent, and cut up into fine pieces before molding. The fabric used varies from fine weave cotton, often shirt trimmings, to coarse canvas. Tire cord is sometimes utilized for special applications. The use of chopped fabric ordinarily requires hand filling of the mold and preforming.

So-called pulp-resin articles are made in several ways by a number of major producers. According to one general type of process, an intimate dispersion of the resin in a kraft pulp slurry is prepared by adding either dry resin or a solution of resin and protective colloid to the wood pulp as it is whipped up in a paper beater. The resin-pulp mixture is filtered off by suction over a wire form shaped like the article to be molded.

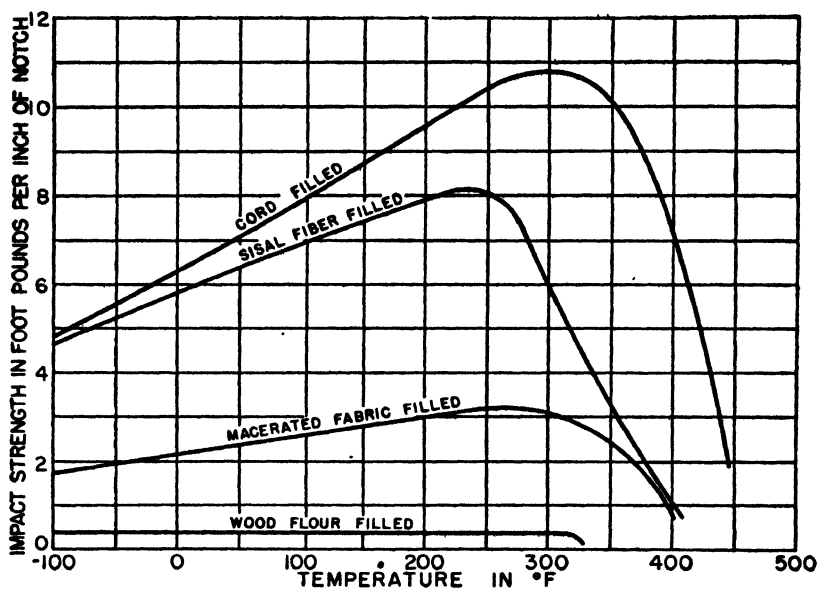


Figure 53. Variation with temperature of notched Izod impact strength of impact grade phenolic molding compositions. (Carswell, Telfair, and Haslanger²⁶)



Courtesy Monsanto Chemical Co.

Figure 54. Experimental beater for preparation of pulp-resin molding compositions.

After a sufficiently thick layer is deposited, it is thoroughly air dried and then molded much as any other preform. In some cases, such as cafeteria trays, several preforms may be telescoped together, resulting in a combined molded-laminated pulp-resin article of excellent strength characteristics whose appearance can be improved by application of an extra heavy surface coat of resin. "Kys-It" is a typical pulp-resin plastic.

A second method of fabricating pulp-resin articles involves the formation of flat sheets or boards from pulp, or sometimes rag fibers, either in the way just described or by impregnation with an alcoholic solution of resin and subsequently molding simple shapes from the dried, flat boards. Blanks of this type, often used as reinforcement for molded articles such as French telephone receivers, are known as "Bakelite Board," manufactured by the Rogers Paper Co. and sold by the Bakelite Corporation. Material of this kind is utilized in matrices for application, in turn, as molds with which to form rubber printing plates, employed especially in printing cotton goods and paper bags. It has also been found possible to chop pulp-resin preforms and use the diced product as a molding compound.

"Co-Ro-Lite" is a similarly prepared product based on long-fibered sisal batting impregnated with phenolic resin. This material is made in apparent densities ranging from 0.71 to 1.33 after molding. In the lower densities it is open and somewhat flexible.

Phenolic impregnated tissue paper, creped in cross directions, is produced for direct compression molding. This new development permits introduction of exceptionally high impact strength into relatively complicated molded articles. Low-pressure molding of impregnated crepe paper, edge wound, has resulted in fabrication of porous oil filters.

While considering organic fillers it should be noted that soybean meal has also been used, but has not yet attained much success, despite glowing accounts in the daily press. Purified soybean protein offers promise of yielding molding powders with improved flow characteristics for general purpose applications, but its acceptance remains for the future.

Since all the fillers just discussed are of organic nature, none of them yields molded articles possessing high heat resistance. For this purpose it is necessary to resort to mineral fillers such as diatomaceous earth or, still better, mica or asbestos. The latter is more common than mica. There are many grades of all these materials and other inorganic powders as well, and the properties of molding compound vary with the specific filler chosen. In the case of asbestos, for example, the longer the fiber, the greater is the impact strength; likewise greater are difficulties of preparation and molding. Iron-free, acid-washed asbestos is sometimes used in electrical applications where the inferior electrical properties of the

more customary asbestos filled materials are inadequate. Both arc-resistance and water-resistance are improved without seriously impairing

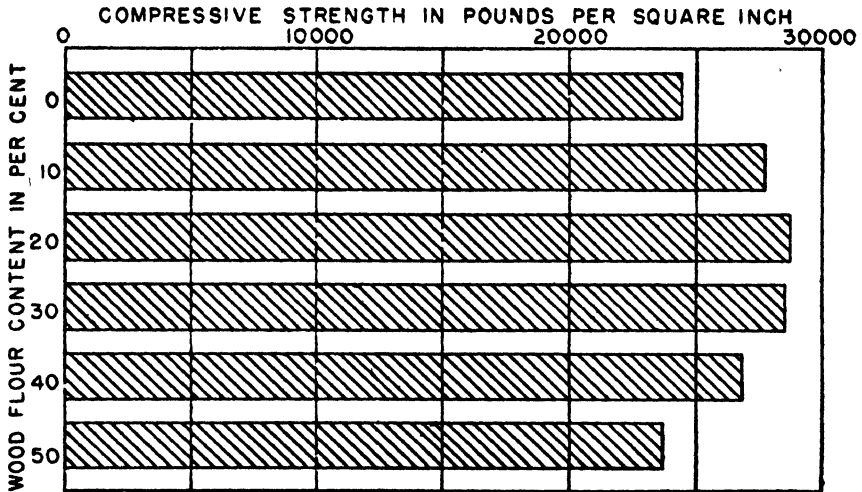


Figure 55. Effect of filler content on compressive strength of wood flour filled phenolic moldings.

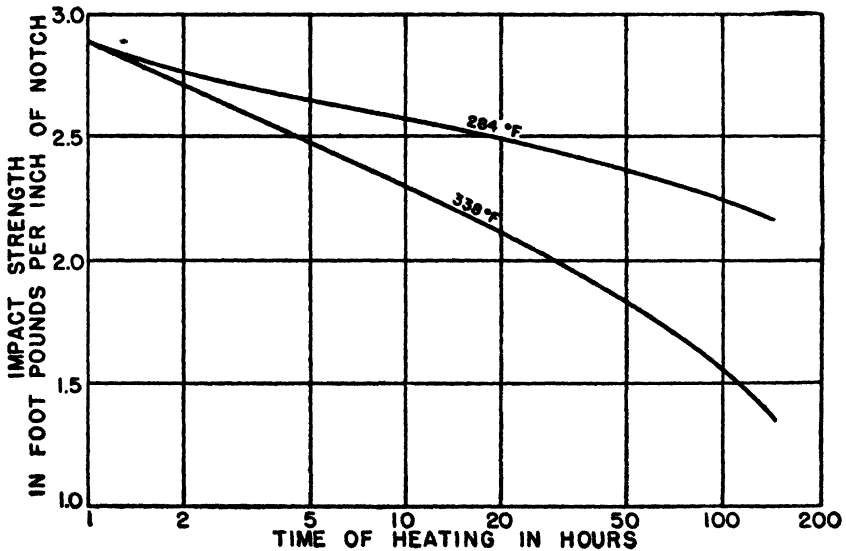


Figure 56. Effect of continuous heating on impact strength of molded bars of fabric filled phenolic. (Carswell and Nason²⁵)

strength by first driving off water of crystallization from the asbestos at a red heat.

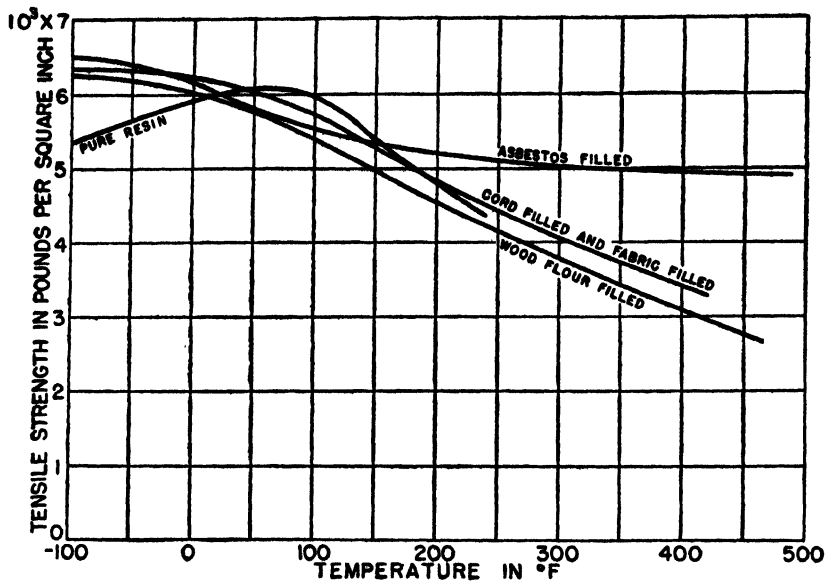


Figure 57. Variation with temperature of ultimate tensile strength of variously filled phenolics. (Adapted from Carswell, Telfair, and Haslanger²⁶)

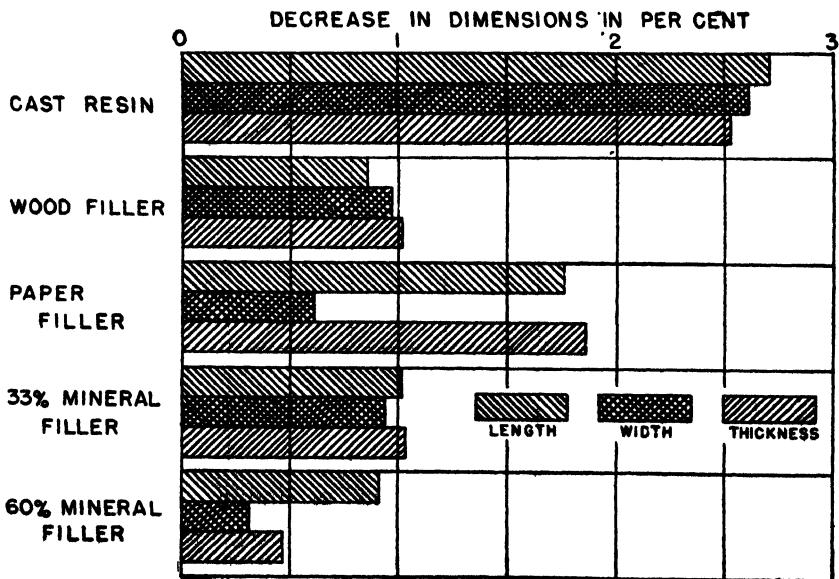


Figure 58. Decrease in dimensions of variously filled phenolic moldings after exposure to dry heat at 110° for 21 days. (Adapted from Halls⁴⁰)

Mica is used as a filler to improve heat resistance, dimensional stability, and electrical properties, especially for low loss applications. It is superior to untreated asbestos for this type of service and, at the same time, imparts excellent water resistance.

Graphite is commonly used to improve frictional characteristics of phenolic parts. Electrical conductivity is, of course, increased thereby.

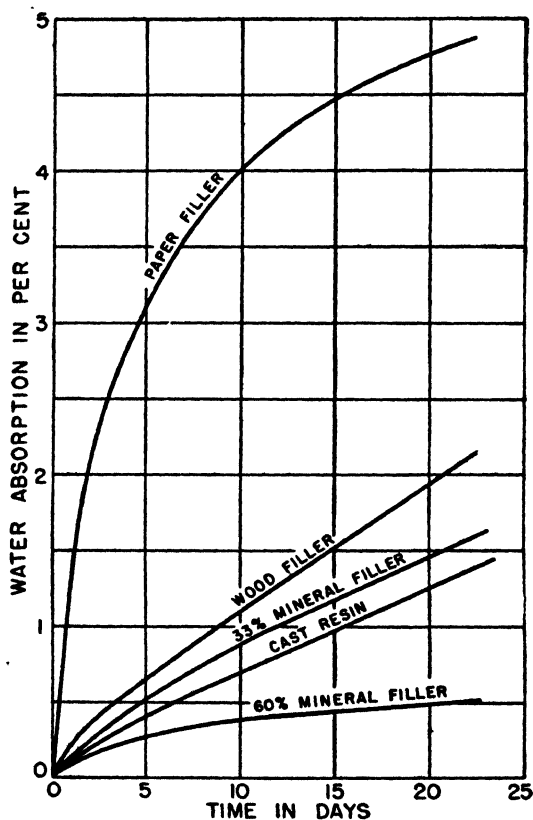


Figure 59. Effect of filler on the water absorption at 20° of molded phenolics. (Mineral filler in the case of 60 per cent loading: mica.) (Halls⁴⁰)

Properties. Both the amount and type of filler affect the physical properties of the molded article. The relation between wood flour content and compressive strength, for example, is illustrated in Figure 55. The influence of the kind of filler upon impact strength has been discussed in the preceding section. Impact strength of molded phenolics is impaired by prolonged heating, as shown in Figure 56. Various relations between the type of filler and other physical properties are shown in Figures 57 to 59.

Properties of various grades of these products can best be illustrated

Table 5.* Detail Requirements for Test Specimens Molded from Phenolic Molding Compounds*

	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10
Water absorption, max. weight gain, per cent	0.15	0.80	0.80	1.50	1.75	1.75	0.07	0.07	0.20	0.10
Specific gravity, 25/25 (77/77F), max.	1.27	1.45	1.42	1.45	1.45	1.45	2.00	2.00	1.95	1.95
Flexural strength, min., psi	12,000	9,000	9,000	9,000	9,000	9,000	8,000	8,000	9,000	7,500
Impact strength (Izod), min., ft-lb per in of notch	0.36	0.24	0.34	0.80	1.75	4.00	0.30	0.30	0.70	0.25
Tensile strength ($\frac{1}{2}$ -in specimen), min., psi	7,000	7,000	7,000	5,500	6,000	6,000	5,500	5,500	4,500	5,000
Compressive strength, min., psi	—	25,000	25,000	25,000	25,000	25,000	15,000	15,000	15,000	15,000
Mold shrinkage, in per in	—	—	—	—	—	—	—	—	—	—
Insulation resistance, min., megohms	0.010	0.006	0.005	0.002	0.003	0.004	0.001	0.001	0.001	0.003
Dielectric strength, min., v. per mil	0.014	0.008	0.008	0.007	0.006	0.006	0.004	0.004	0.005	0.006
Dielectric constant, max.	—	—	—	—	—	—	—	—	—	—
Power factor, max.	—	—	—	—	—	—	—	—	—	—
Loss factor, max.	—	—	—	—	—	—	—	—	—	—

* For methods of testing see Section 6 of A.S.T.M. Specifications D700.

by quoting the classification and requirements set forth in the A.S.T.M. "Tentative Specifications for Phenolic Molding Compounds (D700—43T)." ^{3, 34} Table 5 lists requirements of ten different types of materials which differ chiefly in respect to filler as follows:

"Type 1. An unfilled transparent or translucent material suitable for both electrical and mechanical applications.

"Type 2. General purpose wood-flour-filled material suitable for both electrical and mechanical applications.

"Type 3. General purpose material with a cellulose filler which may be wood flour or cotton flock. It is somewhat higher in impact strength than Type 2 and suitable for both mechanical and electrical applications.

"Type 4. Moderate impact strength material with cotton rag or other suitable forms of cellulose filler to give the required strength for this type.

"Type 5. Medium impact strength material with cotton rag or other suitable forms of cellulose filler to obtain the required strength for this type.

"Type 6. High impact strength material with cotton rag or other suitable forms of cellulose filler to obtain the required strength for this type.

"Type 7. An electrical high-frequency low-loss material with a mineral filler.

"Type 8. A superior electrical high-frequency low-loss material with a mineral filler.

"Type 9. General purpose mineral-filled material for both electrical and mechanical applications.

"Type 10. Heat-resistant mineral-filled material."

Table 6 shows certain characteristics of molded pulp-resin preforms as compared with standard high pressure impact resistant molded phenolics. Table 7 indicates the relation between resin content and these properties

Table 6. Comparison of Physical Properties of Pulp-Resin Preforms Molded at 880 PSI and Standard High Impact Molding Compounds Molded at 3000 PSI ⁴²

Material	Resin Content (%)	Tensile Strength (psi)	Flexural Strength (psi)	Impact Strength Notched-Isoad (ft-lb/in of notch)	Water Absorption 24 hr (%)
Kraft pulp-resin preform	55	13,400 ± 1130	18,200 ± 1050	1.09 ± 0.00	0.42
60% pulp, 40% macerated fabric-resin preform	55	13,500 ± 689	16,100 ± 1300	2.34 ± 0.03	0.60
Macerated fabric-resin preform	55	9,500 ± 705	16,200 ± 490	3.00 ± 0.08	0.31
Macerated fabric filled molding compound	50	5,500 ± 855	10,200 ± 550	3.50 ± 0.13	1.67
Cotton cord filled molding compound	50	4,800 ± 625	12,400 ± 1050	8.00 ± 0.18	1.91

Table 7. Influence of Resin Content on Physical Properties of Kraft Pulp-Phenolic Resin Preforms Molded at 800 PSI and 320° F ^a

Resin Content (%)	Tensile Strength (psi)	Flexural Strength (psi)	Impact Strength Notched Isod (ft-lb/in of notch)	Water Absorption 24 hr (%)
55	13,400 ± 1130	18,200 ± 1050	1.09 ± 0.18	0.42
45	13,500 ± 1170	16,400 ± 710	2.72 ± 0.16	0.64
35	12,600 ± 1140	18,600 ± 1365	4.80 ± 0.57	0.82
25	12,600 ± 330	15,200 ± 575	6.64 ± 0.78	24.3
15	12,200 ± 1030	14,000 ± 740	6.96 ± 0.64	70.6

in the case of pulp-resin products. Table 8 shows the dependence of physical properties upon the type of fiber used in the preform.

Applications. Applications of molded phenolics are determined primarily by their physical properties which, to a considerable extent, are contingent upon the filler. Prior to Pearl Harbor, by far the largest number of molded articles were made from general purpose, wood flour filled compounds. Electrical insulating characteristics of these materials are good, although they are subject to tracking and should not be used for high voltage applications. While their heat resistance is not as high as that of asbestos filled products, it is sufficiently good for such ordinary uses as electric light sockets, plugs, and switches. Moisture absorption is also good enough for most general purpose electrical applications, although those uses which demand extreme moisture resistance and rigid dimensional stability in the presence of water at elevated temperature require other fillers, such as schist mica. Typical applications of general purpose phenolics include boxes, closures, novelties, machine parts, housings, electrical appliances, office equipment parts, camera cases, handles, knobs, radio tube bases, switch plates, wall plugs, door knobs, pencil barrels, housings for door chimes, house numbers, razor cases, and radio cabinets.

Prior to World War II, about 90 per cent of all molded phenolics were of the general purpose, low impact type. Military requirements caused such an increase in demand for materials of moderately good or high impact that, in 1942, some 60 per cent of the molding materials produced in this country possessed improved shock resistance as compared with general purpose, wood flour filled materials.

Cotton flock filled phenolics find application where impact strength requirements are higher than can be satisfied by general purpose compounds. One hundred per cent cotton-filled materials show relatively high impact strength, as illustrated by telephone parts, typewriter space bars, housings and tool parts which are molded from such material. For still more severe applications, such as conduit elbows or bubble caps

Table 8. Effect of Fiber Type on the Physical Properties of Fiber-Resin Preformed Material¹⁴

Preformed Fiber Resin	Resin Type and Content	Molding Pressure (psi)	Specific Gravity	Flexural Properties			Edgewise Compressive Strength (psi)	Impact Strength (Notched Isod)		Tensile Strength (psi)	Water Absorption (%)
				Parallel*	Deflection (inches)	Flexural Strength (psi)		Perpendicular	Parallel†		
Kraft (unbleach)	45% Resinox 635	2200	1.33	17,140 ± 1008	0.081	17,120 ± 676	27,400 ± 333	3.11 ± 0.10	0.85 ± 0.05	11,400 ± 740	0.58
	45% Resinox 635	2200	1.35	17,100 ± 700	0.071	19,300 ± 775	25,540 ± 804	1.91 ± 0.09	0.85 ± 0.03	11,260 ± 1243	0.43
Defibered Rag	45% Resinox 635	2200	1.35	17,000 ± 775	0.097	16,200 ± 533	26,400 ± 1200	2.67 ± 0.15	1.54 ± 0.04	10,000 ± 320	0.66
	45% Resinox 635	2200	1.35	15,930 ± 252	0.067	15,260 ± 328	26,500 ± 1300	2.69 ± 0.32	0.78 ± 0.04	9,500 ± 480	0.69
Ground Wood	45% Resinox 635	2200	1.34	11,800 ± 220	0.055	10,820 ± 234	22,400 ± 1243	1.21 ± 0.07	0.55 ± 0.04	8,400 ± 809	0.43
	45% Resinox 635	2200	1.35	11,600 ± 1732	0.044	12,320 ± 864	28,000 ± 943	1.54 ± 0.09	0.61 ± 0.21	8,100 ± 807	0.55
Asbestos Glass Fiber 85-15	45% Resinox 635	2200	1.72	17,700 ± 525	0.050	17,970 ± 1155	27,000 ± 640	2.94 ± 0.19	2.10 ± 0.05	9,300 ± 1400	0.14

* Broken parallel to Molding Pressure.

† Notch runs parallel to Molding Pressure.

for distillation towers, chopped fabric fillers are employed. Two-way creped paper, impregnated with resin and molded, has already been mentioned. This is a new development and applications have been largely military.

Impregnated sisal batting, sold under the trade name "Co-Ro-Lite," can be molded under high pressure by conventional methods or under low pressure by the rubber bag technique. Although rigid, it is somewhat flexible and has therefore found use in solid hubs with flexible peripheries. It is used in abrasive disc backing, in trays, and airplane gas tank baffles. An important military application has been in jettison gasoline tanks.

Important uses of pulp-resin products are in military parts, printing matrices, and cafeteria trays. Plastic outlet boxes of this type are under development. Typewriter frames have been molded experimentally to replace die-cast aluminum.

The much publicized Ford automobile body and such body parts as rear trunk compartment doors have been made from these materials. There is, however, considerable room for discussion concerning the practicability of high-pressure molded all-plastic automobile bodies. In such uses, economic aspects play an important role. One must always ask, "What is to be gained by use of a plastic in place of sheet metal or whatever other material may be employed at present?" As a rule, mere novelty is no justification.

For special electrical applications, molding powders filled with inorganic materials are used, as in automotive ignition parts, rotors, coil tops, distributor caps, and radio condensers.

Asbestos filled phenolics are heat resistant and find application in flat-iron handles, connector plugs, stove parts, and kitchenware handles. Where washed with acid to remove iron or where fired at high temperatures, asbestos fillers may also be used in molded plastics destined for such electrical applications as distributor caps.

Special molding powders find a diversity of applications ranging from jars and valves to rayon equipment, bearings, facings, and coffins.

Especially unique applications are to be found in molded brake linings and abrasive wheels where phenolic resins serve as binders for the main body of the article. Other materials of resinous nature, such as hard rubber, may be combined with phenolics in these vitally important uses.

Military applications of molded phenolics have been legion. With the important exception of buttons, high impact materials are essential in practically all cases, while extreme ranges of temperature, from arctic to tropic, must have relatively little effect upon shock resistance and other physical properties. Phenolic housings for control devices and navigation instruments such as altimeter gages on planes are invaluable. The dielec-

tric properties of molded phenolics are utilized at many points in radio transmitting and receiving equipment and direction finders of planes, in field telephonic equipment, and in electrical systems of all types of military weapons. Stocks for sub-machine guns are molded from high impact phenolics, as are also nose-pieces for trench mortar shells, hand grenades, training scabbards, jettison gasoline tanks for aircraft and innumerable other articles.

Trade Names and Statistics. Phenolic molding compounds are produced by some fifteen manufacturers. Several of these companies do their own molding; the majority sell to custom molders. Important names are "Bakelite," "Durez," "Heresite," "Indur," "Insurok," "Makalot," "Micaarta," "Resinox," and "Textolite" in the case of phenol-formaldehyde plastics and "Durite" in the case of phenol-furfural compounds. Some of these trade-marks are also applied to other types of plastics; thus, for example, one should specify "Bakelite" phenolic.

Prices run from about 15 cents per pound for general purpose molding powders to about 50 cents per pound for special mineral-filled materials designed for x-ray opacity.

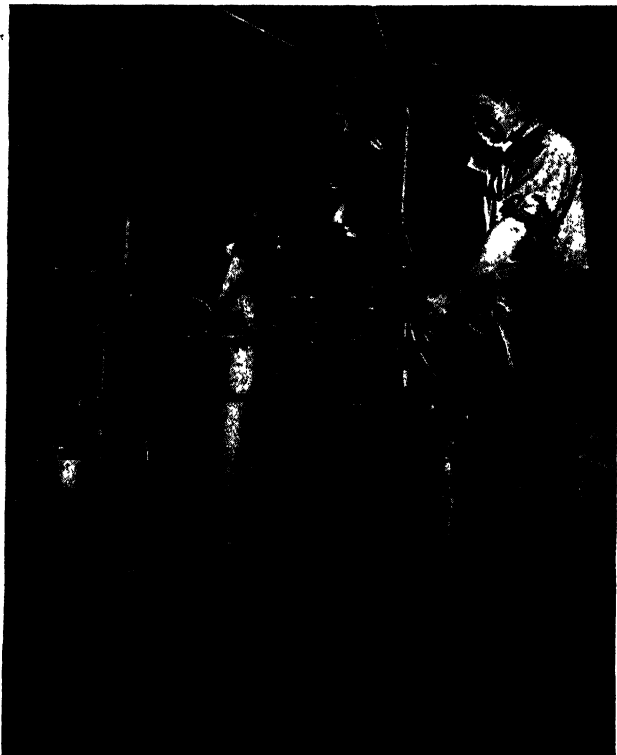
In 1943, approximately 60,000,000 pounds of phenol-formaldehyde resins, not including fillers, were consumed in the manufacture of phenolic molding powders.

Laminated Articles

Manufacture. In the very early days of the phenolic resin industry, phenol was used for the production of laminating varnishes. During World War I, however, the demand for this chemical in explosives of the picrate type was so great that efforts were made to develop cresylic acid cuts for laminating applications. It was found that these intermediates were, in fact, superior to phenol itself from the point of view of yielding resins of longer curing time, an advantage in laminating technique. Until the entry of the United States in World War II, therefore, cresylic acid cuts, substantially free of *o*-cresol, remained the chief intermediates used in laminated materials. Because of the demand which arose after Pearl Harbor for increased production of plasticizers and other chemicals derived from the cresols, a marked shift back toward the use of phenol itself has occurred during the past few years.

The manufacture of laminated products has already been discussed and illustrated in Chapter 5. Phenol or cresylic acid is first admixed with formalin and with ammonia, the latter serving as catalyst. The reaction mixture is heated until resinification has proceeded well into the soluble A-stage and vacuum is then applied to remove most of the water. Alcohol is added directly to the reactor and the resultant solution is cooled and

transferred to troughs through which sheet material—paper, cloth, asbestos paper, asbestos cloth, or glass fabric is passed. The solvent is evaporated and the impregnated sheet material is then wound up on rolls and subsequently cut to size. Cut sheets are superimposed upon each other, the total required to yield a given thickness being determined by weight. The piles of impregnated sheets are then compressed under heat.



Courtesy Westinghouse Electric & Mfg. Co.

Figure 60. Reaction kettle where phenolic laminating resin is thinned to a consistency that will permit it to saturate the paper or cloth base.

As a rule, lamination is carried out at temperatures of about 160 to 190° and under pressures of 1000 to 2000 pounds per square inch. To avoid blistering, pressure should be maintained not only during heating and curing operations, but also while cooling. For a typical laminating cycle, reference should be made to Chapter 5.

Rods and tubes are fabricated by comparable processes in which the sheet material is wound about mandrels, under heavy roller pressure, before curing. In the case of rods, the mandrel is small and is removed be-

fore molding under heat and pressure. Where tubes are to be made, the mandrel is first covered with a specially selected grade of waxed paper and the laminate is cured before the core is removed, the waxed paper facilitating its subsequent elimination. Tubes may be molded under heat and pressure comparable to conditions given above, or they may be simply baked without pressure. In the latter case, there is some minor porosity of the finished plastic so that its density is slightly lower and its water absorption somewhat greater than in the case of pressure-molded tubes. Oven-baked tubes can be distinguished from those molded under high pressure by lack of surface luster and absence of mold parting lines. Tubes are occasionally wound spirally.

Angles, channels, and zees are also available in standard shapes and sizes from several manufacturers.

In the production of decorative sheets from laminated phenolics, the top layer may be of paper or cloth printed or dyed in any appropriate design and color. Light shades can be obtained by using a urea-formaldehyde or melamine-formaldehyde resin in place of phenolic. In order to provide special properties, such as resistance to cigaret burns for café table tops, a thin sheet of metal, usually perforated, may be imbedded beneath the surface layer in order to conduct heat away quickly from localized spots. Use of metal inlays further broadens decorative possibilities.

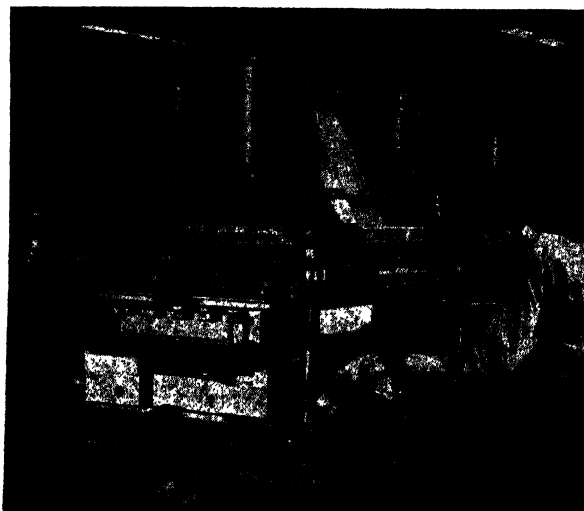
Although thermosetting plastics are commonly said to be completely cured and therefore refractory to forming after lamination is completed, it has recently been found possible to impart relatively simple shapes to laminated phenolic sheet by heating to about 300° F and forming over wood or other simple molds. Heating may be conveniently carried out in oil or other fluid media or it may be carried out dry by means of infrared. Reverse curves may even be formed with care. For such fabricating procedures, although fully cured stock may be employed, it is preferable to use laminates which have been only partially cured, subsequently completing the cure, if necessary, in an oven. Special resins suitable for laminates destined for post-forming are now available. Greater ease of forming is achieved by use of loosely woven or knitted fabric bases. Paper laminates are more difficult to post-form than fabric base materials, accepted radius-to-thickness ratios for these two general classes of laminates being 15 and 3.5 respectively.

Properties. Laminated phenolics have been used for many years in innumerable industrial applications. Even before phenolic resins were known, the electrical industry made use of laminated boards impregnated with shellac and copal which possess excellent electrical insulating characteristics below about 70°, at which temperature these natural resins



Courtesy Westinghouse Electric & Mfg. Co.

Figure 61. Heating a laminated phenolic sheet for post-forming prior to molding. The operation shown here is carried out in an infrared oven.



Courtesy Westinghouse Electric & Mfg. Co.

Figure 62. A power press with wooden molds used in post-forming a laminated phenolic aircraft cable guard.

begin to soften. The National Association of Electrical Manufacturers, therefore, was quick to see the advantages of laminated phenolic plastics which could be classified according to standard specifications. NEMA standards have been set up for several grades of laminated phenolics and a nomenclature has been adopted by this organization to which the principal laminators adhere. NEMA grades of laminated phenolic sheet material⁵⁹ are as follows:

"Grade X. A strong paper base laminated material primarily intended for mechanical applications where electrical requirements are of secondary importance. Should be used with discretion when high humidity conditions are encountered. Not equal to fabric base grades in impact strength.

"Grade P. A paper base laminated material primarily intended for punching. More flexible and not quite as strong as Grade X. Moisture resistance and electrical properties intermediate between Grades X and XX.

"Grade XX. A paper base laminated material suitable for usual electrical applications. Good machinability.

"Grade XXP. A paper base laminated material similar to Grade XX in electrical and moisture resisting properties, but more suitable for hot punching. Intermediate between Grade P and XX in punching and cold flow characteristics.

"Grade XXX. A paper base laminated material, suitable for radio frequency work, for high humidity applications, and with minimum cold flow characteristics.

"Grade XXXP. A paper base laminated material similar to Grade XXX, but having lower dielectric losses and being more suitable for hot punching. This grade has greater cold flow than Grade XXX, and is intermediate between Grades XXP and XXX in punching characteristics.

"Grade C. A fabric base laminated material made throughout from cotton fabric weighing over 4 oz per square yard and having a count as determined from inspection of the laminated plate of not more than 72 threads per inch in the filler direction, nor more than 140 threads per inch total in both warp and filler directions. A strong, tough material suitable for gears and other applications requiring high impact. The heavier the fabric base used the higher will be the impact strength, but the rougher the machined edge; consequently, there may be several subgrades in this class adapted for various sizes of gears and types of mechanical service. Should not be used for electrical applications except for low voltages.

"Grade CE. A fabric base, laminated material of the same fabric weight, and thread count as Grade C. For electrical applications requiring greater toughness than Grade XX, or mechanical applications requir-

ing greater resistance to moisture than Grade C. Exceptionally good in moisture resistance.

"Grade L. A fine weave fabric base laminated material made throughout from cotton fabric weighing 4 oz or less per square yard. As determined by inspection of the laminated plate, the minimum thread count per inch in any ply shall be 72 in the filler direction and 140 total in both warp and filler directions. For purpose of identification, the surface sheets shall have a minimum thread count of 80 threads per inch in each of the warp and filler directions. This grade is suitable for small gears and other fine machining applications, particularly in thickness under $\frac{1}{2}$ inch. Not quite as tough as Grade C. Should not be used for electrical application except for low voltage.

"Grade LE. A fine weave fabric base laminated material of the same fabric weight, and thread count as Grade L. For electrical applications requiring greater toughness than Grade XX. Better machining properties and finer appearance than Grade CE—also, available in thinner sizes. Exceptionally good in moisture resistance.

"Grade A. An asbestos paper base laminated material. More resistant to flame and slightly more resistant to heat than other laminated grades because of high inorganic content. Suitable for only low voltage applications. Minimum dimensional changes when exposed to moisture.

"Grade AA. An asbestos fabric base laminated material. Similar to Grade A but stronger and tougher. Minimum dimensional changes when exposed to moisture."

Properties of laminated phenolics are typified by those of various grades of "Micarta," listed in Table 9.

Applications. Phenolic laminated plastics offer almost unlimited possibilities in decoration because of the variety which can be obtained in color and pattern of the surface sheet. Their utility in the construction of table tops, counters, and show cases for restaurants, cafés, and stores is well known. Their use in modern design is exemplified by the dining cars and lounges of the Twentieth Century Limited, in which they have been extensively employed. They have found use in the panelling of lobbies, offices, and even store and theater fronts. Shaped laminated door panels for domestic refrigerators have been introduced.

Electrical applications of laminated phenolics have already been mentioned. Unusually severe service conditions, such as insulating panels in battleships where extraordinary strength and impact resistance are required have been met by glass fiber fabric base laminated phenolics.

Laminated phenolics have proved invaluable in much industrial equipment. The silent gear of the automobile timing train no longer has any element of novelty. Phenolic gears, both large and small, are common-

Table 9. Mechanical and Electrical Properties of Laminated "Micarta" 85

Micarta Grade No.	200	213 423	219 429	221A 431A	222 432	223	238 448	239	254 464	262	271	273	280	281	286 496	295	400	872
NAVY TYPE	FBH	PBM	PBG	FBE	PBE	---	FBI	PRH	PBE	FBM	---	---	---	---	FBG	---	---	NDP
NEMA GRADE	AA	X	XX	LE	XXX	---	L	A	XXX	C	---	---	---	---	CE	---	---	NDP
ANST TYPE	IV-AA	I-X	XX	II-LE	I-XXX	---	I-L	I-VA	I-XXX	II-C	---	---	---	---	II-CE	---	---	NDP
SPECIFIC GRAVITY	1.8	1.35	1.35	1.35	1.35	1.38	1.38	1.35	1.38	1.38	1.72	1.35	1.46	1.38	1.35	1.72	1.38	1.38
DENSITY (Pounds per cubic inch)	.085	.049	.049	.049	.050	.050	.049	.065	.049	.065	.062	.049	.053	.050	.049	.062	.050	.050
MOSURE ASSORPTION	1.5	6.0	2.0	1.5	4.0	1.5	2.5	2.5	1.2	4.5	2.4	0.9	5.2	1.2	1.8	3.2	4.5	3.0
(% Increase in Weight)	1.0	3.2	1.3	0.9	2.0	1.4	1.7	1.0	0.9	2.5	1.5	0.6	2.8	0.9	1.3	2.0	2.5	2.0
1" X 3" Thk. 24 hr. @ 25°-A.S.T.M.	0.5	1.1	0.5	0.55	1.1	0.7	1.1	0.5	0.5	1.2	1.0	0.4	1.5	0.6	0.7	1.3	1.5	1.0
MOSURE ASSORPTION AT SATURATION (1" X 3" X 1/16")	4	15	8	5	8	4	6	4	6	7	6	3	13	4	6	9	7	9
(% Increase in Weight)	12,000	16,000	11,000	13,000	8,000	11,500	14,500	13,000	13,500	10,000	9,000	7,000	7,000	9,000	13,000	8,000	11,500	13,000
TENSILE STRENGTH (Pounds per sq inch)	CG	11,000	8,000	9,500	6,000	7,000	10,000	10,000	10,500	11,000	1,000	6,000	9,000	6,000	12,000	8,000	7,000	9,000
MODULUS OF ELASTICITY (Tension C—Times 10 ⁶)	WG	1.3	1.7	1	.9	1.0	1	1	1	1	1	.8	.6	.8	1	.9	.6	1.6
COMPRESSIVE STRENGTH (Pounds per sq inch)	E	49,000	38,000	31,000	38,000	22,000	37,000	40,000	36,000	40,000	35,000	40,000	32,000	36,000	40,000	37,000	36,000	43,000
MODULUS OF ELASTICITY (Compressive—Times 10 ⁶)	E	7	7	6	6	6	5	6	7	5	7	5	4	4	6	5	5	5
FLXURAL STRENGTH (Pounds per sq inch)	F	25,000	27,000	17,000	20,000	13,000	19,000	21,000	15,000	20,000	15,200	17,500	12,200	14,000	21,000	14,500	18,500	11,200
MODULUS OF ELASTICITY (Flexural—Times 10 ⁶)	F	24,000	27,000	14,000	21,000	11,000	17,000	19,000	12,500	20,000	17,500	9,400	12,800	10,000	20,000	14,800	10,000	10,600
SHEAR STRENGTH (Pounds per sq inch)	ECG	24,000	26,000	15,000	18,000	11,000	18,000	17,000	16,000	20,000	14,800	15,500	11,700	14,000	21,000	13,500	17,500	16,800
MODULUS OF ELASTICITY (Shear—Times 10 ⁶)	ECG	12,000	9,000	7,000	11,000	6,000	9,500	7,500	6,000	11,000	9,200	11,000	8,400	10,000	10,000	8,300	7,000	8,000
IMPACT STRENGTH (Charpy-method; foot pounds per inch; unnotched specimen 1/2" thick)	F	12.3	2.9	4.5	10.4	7.2	9.1	5.5	3.3	15.8	11.0	5.1	25.0	6.3	13.2	7.0	9.5	4.9
ROCKWELL HARDNESS (Load in lbs, sample 1" X 1" X 1/2")	F	106	114	112	113	104	112	106	111	102	102	115	90	111	108	93	106	118
DIELECTRIC STRENGTH (Short time method, V./mil)	E	102	108	106	106	98	109	99	101	97	97	108	74	107	101	89	98	108
DIELECTRIC STRENGTH (Step by step method, V./mil)	E	30	60	60	80	50	50	30	60	50	70	60	60	50	50	200	130	640
DIELECTRIC CONSTANT (10 ⁴ cycles)	E	60	300	350	250	450	200	175	60	450	230	250	150	200	225	130	100	370
POWER FACTOR (Per cent at 10 ⁴ cycles)	E	6.6	6.5	5.5	5.0	5.3	5.7	5.8	6.1	5.5	5.8	5.5	5.6	5.1	5.3	6.0	6.4	6.6
	30 +	7.0	4.5	4.5	6.0	6.5	7.8	12	3.5	6.6	5.9	4.5	7.0	4.4	5.0	5.4	7.8	4.5

WG: with grain; CG: cross-grain; F: flatwise; E: edgewise

place on numerous machines. Laminated phenolic bearings have become standard equipment in much heavy machinery, especially where water can be used as lubricant. In rolling mills, the life of phenolic bearings is often from ten to thirty times that of babbitt metal or bronze. In the paper industry, where large volumes of water are handled, not only bearings, but doctor blades, table rolls, forming boards, and suction box covers are made from laminates.

The combination of strength and light weight of these materials has led to important applications in airplane production. There are several



Courtesy Westinghouse Electric & Mfg. Co.

Figure 63. Infrared drying of "Micarta" army helmets in 95 seconds as compared with 15 minutes by the oven method. During the war, these plastic liners were dried at the rate of 500 an hour by this means.

hundred laminated phenolic pulleys in the control mechanism assembly of every transport and military plane. Fairleads, propeller supports, cabin air controls, body struts, and reinforcing elements for gas tanks are other aircraft applications of these materials.

Molded-laminated miners' and firemen's helmets have been manufactured for several years. Liners for military helmets are of more recent development, in the production of which low-pressure molding methods have been applied.

The use of fluorescent dyes and pigments is an innovation which has resulted in laminates that fluoresce under ultraviolet light. Phosphorescent

laminates are also available. Fluorescent laminated instrument panels are now standard installations in military planes.

Low-Pressure Laminates. Following the entry of the United States into World War II, the demand for large molded plastic parts increased rapidly. Aircraft manufacturers were especially active in seeking large moldings—a search which led to the development of so-called low-pressure and no-pressure molding methods. Phenolic resins are available for low pressure molding in Kirksite (cast zinc alloy) or analogous molds where pressures up to about 250 pounds per square inch are employed. It has also been found that some of the older laminating resins can be used for no-pressure molding-laminating at contact pressures only. Principal applications have thus far been chiefly military, such as non-structural aircraft parts and helmet liners.

It has been found that the best strength characteristics are obtained in low-pressure laminates by use of glass fabrics as a base material. Another very useful base material has appeared in the form of Mitscherlich and analogous high-strength papers. Initial work in the latter development was carried out at the U. S. Forest Products Laboratory. Several paper companies are now manufacturing high strength products for plastics application. For the most part these materials are special sulfite papers in which cellulosic degradation has been held to a minimum and in which the fibers are oriented in one direction. In order to obtain products with approximately homogeneous strength characteristics, high strength paper laminates must be built up by crossing successive layers at right angles to each other, for strength within an individual sheet is greatest in the direction of orientation.

Mechanical properties of typical high-strength paper base laminates are given in Table 10. It will be noted, for example, that tensile strength values are approximately double those previously given for the customary Grade X high-pressure paper base laminates. Glass fabric yields laminates possessing still higher strength characteristics, ultimate tensile strength values reaching 37,000 pounds per square inch or more.

Trade Names and Statistics. Resins and varnishes for laminating purposes are available from the makers of molding powders under the same trade designations as have been given above. High-pressure laminated sheets, rods, and tubes are produced by some fifteen concerns, many of whom make their own resins. These same companies carry out limited molding-laminating operations, such as fabrication of pulleys and hats, while they also supply finish-machined laminated articles like gears and washers. Best known trade names of high-pressure laminates are "Aqualite," "Dilecto," "Duraloy," "Formica," "Insurok," "Lamicoid," "Mica," "Panelyte," "Phenolyte," "Spauldite," "Synthane," "Taylor," and

Table 10. Mechanical Characteristics of High-Strength-Paper Phenolic Laminates⁴⁸

Property	Paper-base Plastic	
	Parallel Laminated	Cross Laminated
Specific gravity	1.35-1.40	1.35-1.40
Tension		
Ultimate, with grain, psi	35,000	25,000
Ultimate, across grain, psi	18,000	25,000
Modulus of elasticity, with grain, psi	3,000,000	2,300,000
Modulus of elasticity, across grain, psi	1,500,000	2,300,000
Compression		
Ultimate, edgewise with grain, psi	19,000	18,000
Ultimate, edgewise across grain, psi	17,000	18,000
Ultimate, flatwise, psi	40,000	40,000
Flexure		
Modulus of rupture, with grain, psi	32,000	26,000
Modulus of rupture, across grain, psi	20,000	26,000
Modulus of elasticity, with grain, psi	3,000,000	2,000,000
Modulus of elasticity, across grain, psi	1,500,000	2,000,000
Shear		
Edgewise, across grain, psi	13,500	13,000
Edgewise, with grain, psi	13,000	13,000
Flatwise, across grain, psi	12,500	11,500
Flatwise, with grain, psi	11,000	11,500
Bearing—mean values		
With grain, psi	30,000	30,000
Across grain, psi	30,000	30,000
Hardness, Rockwell	M 100	M 100
Water absorption (24 hr total immersion)		
$\frac{1}{8} \times 1 \times 3$ in specimen (unsealed edges), per cent	3-4	3-4
$\frac{1}{8} \times 1 \times 3$ in specimen (sealed edges) per cent	1-2	1-2

Remarks: (1) Material is not affected by oil or high octane gasoline.

(2) The above values may be used for design.

"Textolite." Most manufacturers specialize in industrial laminates. Impregnated paper and fabrics for laminating are also available from several manufacturers.

Low-pressure laminates are fabricated by a considerable number of aircraft, marine, and other manufacturers using special resins available under such trade names as "Bakelite," "Durez," and "Resinox."

Prices vary widely, depending upon thickness, permissible tolerance, quantity, shape, and base material used in laminating. Average figures for $\frac{1}{8}$ -inch sheet material in lots of 300 pounds or over are: paper base—60 cents per pound, cotton fabric base—\$1 per pound, asbestos fabric base—\$1.20 per pound. Prices of low pressure laminating resins average 25 to 35 cents per pound.

In 1941, some 50,000,000 pounds of phenolic resins were used in the manufacture of laminated products.

Plywood

Closely allied to laminated phenolic is resin-bonded plywood. First introduced to this country in 1930 by imports from abroad, American production began in 1935. (Several other synthetic resins—notably ureas—are also now used in the manufacture of plywood.)

In the production of this material, little compression occurs. Veneers are simply bonded together by use of an appropriate adhesive, with or without heat, at pressures which do not usually exceed 200 pounds per square inch—sufficient to ensure intimate contact of the surfaces of the



Courtesy The Resinous Products & Chemical Co.

Figure 64. "Tego" resin film is interleaved between veneer to prepare assemblies for hot-pressing. Each veneer assembly is taped at the edge to permit ease of press loading and handling.

veneers, but insufficient to alter the nature of the wood. Phenolic resin-bonded plywood so made resembles in appearance and performance plywood fabricated with such conventional adhesives as animal or casein glue, blood albumin, or soybean protein. It possesses superior characteristics in so far as the resinous bond is concerned because of water resistance, as well as strength and vermin resistance. It is possible to boil phenolic bonded plywood indefinitely in water without deterioration of the bond. Older adhesives derived from natural glues are more or less water soluble and yield plywoods which delaminate after a few minutes of immersion in boiling water.

In accordance with standard practice in all plywood manufacturing, the grain of the veneers is usually crossed in alternate layers, in order to give a product of fairly homogeneous strength characteristics. The thickness

of the veneers and the kind of wood employed can be varied within wide limits and in numerous combinations.

There are three principal ways of fabricating resin-bonded plywood. The first and oldest method is to insert, between successive wood veneers, sheets of very thin tissue paper which have been impregnated with phenolic resin and dried free of solvent. These impregnated resin sheets, sold under the trade name "Tego" film, contain about twice as much resin as paper by weight. Bonding is then carried out by means of heat and



Courtesy The Resinous Products & Chemical Co.

Figure 65. The "Tego"-veneer assemblies, placed between aluminum cauls, are inserted in the hot press. Here, temperatures of 280–320° F and pressures of 200 psi cure the resin, producing waterproof plywood.

relatively low pressure. In the second method, a solution of phenolic resin is spread onto each of the contacting surfaces of wood veneers, solvent evaporated, and bonding again carried out by means of heat and low pressure. In both of these methods, the moisture content of the wood must be carefully controlled within precise limits—usually about 5 per cent in the first method and from 7 to 10 per cent in the second. These moisture contents are essential for proper flow of the resin and good bonding at the time of heating.

Shaped articles can be fabricated from resin-bonded plywood by forming the veneers over relatively simple molds during the curing operation. So-called rubber bag methods have proved especially effective in the shaping of airplane noses and fuselages for trainer planes. These methods

consist of laying out the laminated veneer over a wood or other inexpensive form and enclosing the whole system within a rubber bag which is then evacuated, forcing the veneer against the inner form. Baking is carried out while the bag is still evacuated. The finished, bonded plywood retains the shape imparted at the time of curing. This, essentially, is the method of the so-called "Vidal" or "Duramold" process. A similar procedure involves the inverse operation of curing while the plywood is forced against an outer frame by means of an inflated rubber bag within. Figure 36 gives a diagrammatic sketch of bag molding methods.

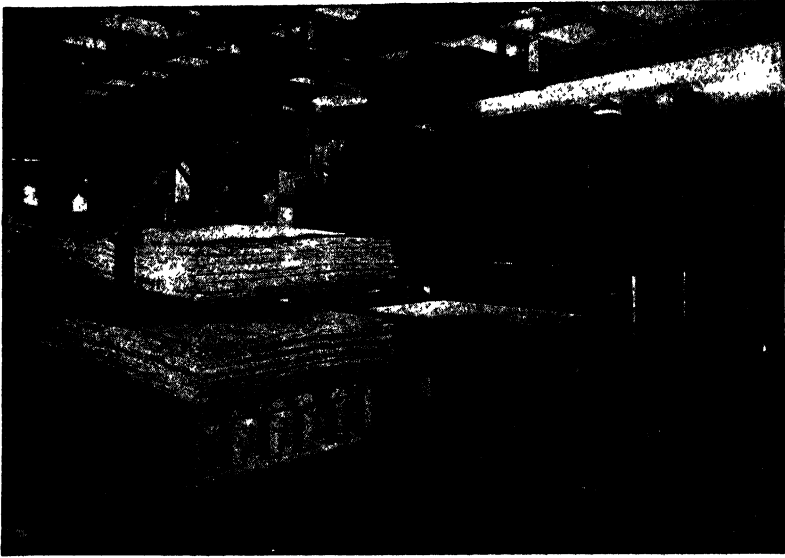


Courtesy The Resinous Products & Chemical Co.

Figure 66. For the manufacture of compound curved plywood sections, the bag molding technique is used. Here layers of veneer and "Tego" resin film are being laid up to form one-half the fuselage of a Fairchild airplane. An inflated rubber bag placed inside the mold applies heat and pressure. Steam lines also heat the concave face of the mold.

A third, relatively new way of manufacturing resin-bonded plywood is by utilizing a phenolic resin solution capable of being cured at room temperature upon addition of a catalyst. While pressure is required, the necessity for heat is eliminated. Adhesives based upon resorcinol, such as "Penacolite," offer considerable promise here.

Resin-bonded plywoods have found wide acceptance in marine, automotive, and constructional fields. A tremendous future is in store for these materials in civilian and industrial applications. Military uses during World War II were spectacular. Army chests, packing cases, field kits, pontoons, and all sorts of furniture for cantonments were made of resin-bonded plywood. Millions of feet of this material—even panels eighty feet in length—have been used in ship construction especially in motor torpedo boats. Plywood flooring, control surfaces, and leading



Courtesy The Girdler Corp.

Figure 67. Two loads of veneer, with electrode between, are ready to roll into the press for the manufacture of plywood by the use of "Thermex" high frequency heat.



Figure 68. Removing plywood cylinders from the mold after curing with "Thermex" high frequency dielectric heating.

Courtesy The Girdler Corp.

edges of wings are standard equipment for many planes. The Glenn L. Martin Co. has equipped bombers with phenolic-bonded plywood bomb bay doors, fourteen feet in length and weighing fifty pounds, built of poplar and mahogany. Millions of feet of flat resin-bonded plywood have gone into the construction of wings, fuselages, bulkheads, gusset plates, and interior surfaces of bombers, pursuit ships, and trainers for both the United States and Great Britain. Resin-bonded plywood fuselages for trainers and twin-motored planes have been manufactured. Plywood noses have been standard equipment on the Canadian Avro-Ansco bomber. The Mosquito fighter-bomber was a plywood plane.

All the methods described above result in resin-bonded plywood whose density is substantially the same as the wood from which it is made. Compressed or compregnated wood (Compreg) consists of layers of wood veneer bonded together under sufficiently high pressure (from 500 to 2000 lbs per sq in) to compress the wood, thus increasing its density and tensile strength proportionately.

The density of compressed wood is about 1.35. One method of manufacture involves lamination of very thin veneers of wood with alternate layers of resin-impregnated tissue paper and bonding under heat and elevated pressure. The product, in which the resin pick-up is 10–15 per cent, is called superpressed plywood. "Tegowood" is a material of this kind. Compressed wood can also be produced by impregnating wood veneers with resin solution, evaporating the solvent, and again bonding under heat and elevated pressure. Resin pick-up in this case is from 25 to 35 per cent. The product is called improved wood. "Pregwood" is of this type.

Compressed wood has become popular in building construction, especially for interior finishing where both its decorative qualities and its improved mechanical, fire-resistant, and vermin-proof characteristics recommend it.

Intermediate in properties between these two types of compressed wood is "Impreg," made by impregnating the veneers and bonding under normal plywood pressures. Here, resin pick-up is in the order of 25 per cent.

Table 11 compares the strength properties of Compreg with those of several other structural materials.

Metal Reinforced Laminates

Allied with laminated products are various combinations of steel with other sheet materials, especially thin veneers of wood. Such metal-backed wood is available commercially where the thickness of wood veneer is as low as 1/85 inch. These products can be bent around corners

Table 11. Comparison of Strength Properties of Compreg, Natural Wood and Common Metals^a

Material	Sp. G.	Mod. of Rupture (psi)	Mod. of Elast. (10 ³ psi)	Compressive Strength (psi)	Shear Strength Maximum (psi)	Izod Impact (ft lb/in)	Mod. of Rupture ÷ S.G.	Compressive Strength ÷ S.G.
<i>Compreg</i> , Parallel grain ^a	1.35	49,000 ^b	4.3	28,000 ^b	4,000 ^d	8	36,000	20,000
<i>Compreg</i> , Cross grain	1.35	22,000 ^c	3.0	20,000 ^c		4	16,000	15,000
<i>Woods</i> (at 12% moisture cont.): ^e								
White Ash	0.58	15,000	1.7	5,600	1,900	—	26,000	10,000
Beech	0.64	15,000	1.7	7,300	2,000	—	23,000	11,000
Birch, sweet or yellow	0.63	17,000	2.1	8,300	2,000	14	27,000	13,000
Sitka Spruce	0.40	10,000	1.6	5,800	1,200	—	25,000	14,000
Douglas Fir	0.44	11,000	1.6	6,700	1,200	—	25,000	15,000
<i>Metals:</i>		Ultimate Tensile Strength					Ultimate Tensile Strength/S.G.	
Cast Brass	8.6	24,000		30,000			2,800	3,500
Cast Iron	7.2	18-60,000		80-150,000			2,400-8,000	11-20,000
Dural	2.8	55-65,000	10	56,000			19-23,000	12,000
Structural Steel	7.8	50-63,000	30	65,000			6,400-8,400	6,400

^a Latest data, Bakelite Laboratories^b In strongest direction parallel^c Parallel to laminæ^d Will vary according to veneers 3000/4000—Single block shear test was used.^e From Forest Products Laboratory, U. S. Department of Agriculture, "Wood Handbook," 1940

of very small radii without cracking. Interior wall panels are thus available which combine beauty of the wood with mechanical strength, fire-proof character, and versatility of steel. These steel-wood combinations have been produced, for example, by uniting wood veneer with "Robertson Bonded Metal." The latter is a specially prepared sheet steel coated with a relatively soft solder which serves as bond for a sheet of cloth partially imbedded therein. The surface layer of the cloth thus mechanically attached to the steel is impregnated with phenolic resin and united with wood veneer or any other desired material by the usual laminating methods.

Miscellaneous Wood-Resin Products

Bonding of wood veneers by means of phenolic resins, either with or without impregnation, has given rise to several other interesting products. United with high-strength paper laminates, combined structural-decorative applications are under development. In these assemblies, it is necessary to be certain that the same weight of veneer is applied to each side of the laminate in order to avoid warpage. Woven impregnated wood veneers, bonded under high pressure and united with any suitable base material, have been developed for decorative panels, ceilings, table tops, and even suitcase coverings and book covers. Such products are sold under the trade name, "Parkwood-Textolite." Still another significant combination of phenolic resins with wood veneers is to be found in wall covering produced by resin-bonding numerous types of wood in thin veneer form to a paper or fabric base which can be applied in much the same manner as wall paper itself.

Cast Phenolics

Manufacture. Cast phenolics have found great favor in costume jewelry and objets d'art because of their clarity, the brilliant colors which can be imparted to them by oil-soluble dyes, and the marbled effects which can be produced by artful use of pigments. Until recently, their use has been restricted to decorative and ornamental fields, but during the past few years they have forced entry into industry. Because their major applications are still artistic in nature, it is especially important to observe caution in the selection of synthetic, high-grade, colorless phenol for their manufacture. All equipment must be constructed of such materials that the reactants will not be contaminated with discoloring impurities which might be introduced by slight reaction therewith. Nickel or nickel-clad apparatus is customary, including pipe lines, valves, pumps, and reaction kettles. An exception is equipment handling formaldehyde. This is made of aluminum.

During their early stages, cast phenolic resins are manufactured in much the same manner as molding and laminating resins, except that the catalyst employed is ordinarily either sodium or potassium hydroxide. According to one process, when resinification has reached a sufficiently advanced point, lactic acid or an analogous acidic material is added to neutralize the alkaline catalyst and, at the same time, yield a salt which



Courtesy Catalin Corp.

Figure 69. Liquid phenolic casting resin being drawn into pouring pot from reaction kettle.

will not precipitate. Most of the water is removed, but not as much as in the case of either molding or laminating resins. Glycerol is then added in order to assist in dispersing the remaining water, as well as that produced upon further condensation. It is essential that the water present in the finished plastic be uniformly distributed throughout. Both the total amount of water and the quantity of added glycerol determine the size of the dispersed globules of water. This globule size, in turn, determines the translucency or opacity of the finished plastic.

Dyes and pigments are added and the resin is usually hand-poured into molds—lead, glass, or latex-coated plaster-of-Paris—where resinification

is completed by standing for periods up to five days at temperatures up to 85°, usually in a heated chamber.

Other types of cast phenolics are produced which contain neither glycerol nor lactic acid salts.

The manufacture of cast phenolics has been further discussed and illustrated in Chapter 5.

Properties. Cast phenolics are available in colors ranging from colorless transparent to marbled black. All colors of the rainbow are obtained in sparkling hues. This is the outstanding fact which fits them for most of their applications. Usually the dimensional stability of cast phenolics is not as good as that of molded products for resinification continues within the plastic over a considerable period of time, resulting in volume changes.

Properties of cast phenolics are exemplified by those of "Catalin," listed in Table 12.

Applications. The bulk of cast phenolics are produced in the form of sheets, rods, tubes, balls, and special rods—square, hexagonal, octagonal, fluted, cloverleaf, etc. From these standard shapes, finished articles are fabricated by machining and polishing. The latter is done by tumbling with shoe pegs or pumice, or by buffing with a muslin wheel. Combs, brush backs, buttons, buckles, jewelry, book ends, smokers' accessories, display fixtures, and ladies' handbag frames are typical applications of cast phenolics machined from stock shapes. Special castings are made in the production of small radio cabinets. The largest all-resin articles yet produced were several figures nine feet high and nine feet across the base, lighted from within, designed by the artist Mancuso and cast in rubber-lined molds for the Federal Building of the 1940 New York World's Fair.

Specially formulated and treated cast resins of superior dimensional stability have been used in the construction of the revolving cap container used on automatic bottle capping machinery, in guide shoes for oil well drilling casings, and in dies used in forming aluminum aircraft parts. Walnut shell flour is often preferred as a filler in such products. Although such industrial applications of cast phenolics have increased recently, they are still limited in number.

Trade Names and Statistics. Cast phenolics were made industrially as early as 1914, but they have become well known only during the past fifteen years. In 1941 they were produced by seven American companies to the extent of 7,000,000 pounds. Trade names are "Bakelite" cast resinoid, "Baker" cast resin, "Catalin," "Gemstone," "Marblette," "Opalton," and "Prystal."

Asbestos-Filled Cast Resins. Unique among phenolic plastics is a product known under the trade-mark "Haveg." Although usually not

Table 12. Properties of Various Grades of "Catalin" *

	A.S.T.M. Test Method	Temp. ° F	R. H. %	General Purpose Decorative Common Values	General Purpose Transparent Common Values	Electrical and Mechanical Common Values	Chemical Resistant Common Values
Specific Gravity				1.375-1.335	1.30-1.335	1.305-1.315	1.390-1.400
Specific Volume—os per cu in				0.751	0.766	0.751	0.90
Refractive Index				1.58-1.61	1.59-1.62	1.59-1.61	1.59-1.61
Light Transmission %				0-5	80-90	0-1	0
Colors				Unlimited	Unlimited	White	Creamy White
Machining Qualities				Excellent	Excellent	Excellent	Excellent
Water Absorption (24 hrs) %				0.5-2.0	0.5-3.0	0.4-0.6	0.1-0.15
Flammability				Non-flammable	Non-flammable	Non-flammable	Non-flammable
Effect of Aging Outdoors				Hardens & Yellows	Hardens & Yellows	Hardens & Yellows	Hardens & Yellows
Effect of Aging Indoors				Hardens & Yellows	Hardens & Yellows	Hardens & Yellows	Hardens & Yellows
Effect of Sunlight				Yellows	Yellows	Yellows	Yellows
Tendency to Cold Flow				None	None	None	None
Tensile Strength, psi	D48-41T	77	50	5,000-9,000	3,000-3,500	8,500-10,000	6,131
Modulus of Elasticity in Tension, psi	D48-41T	77	50	3-6 X 10 ⁵	1.25-4 X 10 ⁵	3.75 X 10 ⁵	
Compressive Strength, psi	D649-41T	77	50	14,000-25,000	4,000-7,000	20,000-25,000	12,885
Flexural Strength, psi	D650-41T	77	50	6,600-9,000	2,950	10,000-12,000	10,887
Maximum Deflection under Flexure, in				0.1	0.12	0.14	
Impact Strength, Izod ft lbs per inch of milled notch	D256-41T	77	50	0.30-0.40	0.30-0.45	0.48-0.60	0.30-0.50
Impact Strength, Charpy Notched ft lbs per in of notch	D256-38			0.27-0.35	0.26-0.31	0.40-0.60	
Impact Strength, Unnotched Charpy ft lbs per in of width	D256-33			3.5	1.6	4 ⁺	
Impact Strength, repeated blows—unnotched—2nd blow				2-3	—	1-4	
Shear Strength, 1 inch Diameter Plunger				4,000-6,000	3,000-4,000	5,000-7,000	
Hardness, Rockwell		77	50	M80-M85	M30-M40	M65-M80	M65-M90
Volume Resistivity, megohm ins	D257-38	77	Dry	1-10 X 10 ¹⁵	1-10 X 10 ¹⁴	1-7 X 10 ¹⁶	
Dielectric Strength, Short Time V/M	D149-39T	77	Dry	300-400	76-98	350-430	300-450

D149-39T	77	Dry	200-350	36-44	260-335	285
D150-41T	77	Dry	15-20	20-30	6.5-7.5	8.9-10.0
D150-41T	77	Dry	12-18	12-15	5.5-6.0	
D150-41T	77	Dry	5-11	7-8	7.4	
D150-41T	77	Dry	0.025-0.2	0.25-0.50	0.10-0.15	0.0210-0.0235
D150-41T	77	Dry	0.1-0.2	0.20-0.30	0.01-0.05	
D150-41T	77	Dry	0.01-0.10	0.09-0.10	0.02-0.05	
D150-41T	77	Dry	2.5-7.5	10-16	0.05-0.9	
D150-41T	77	Dry	1.5-3.0	2.5-4.0	0.17-0.25	
D150-41T	77	Dry	0.8-1.1	0.70-0.80	0.15-0.25	
D495-41	77	Dry	120-140	160-180	200-250	
			1-2.5 $\times 10^6$	0.1-3.0 $\times 10^6$	6.5 $\times 10^6$	
			0.3-0.4			
D648-41T			3-5	8.3-13.0 $\times 10^{-5}$	3-5	4-7
			7.5-15 $\times 10^{-4}$	95-113° F	8.1-10.9 $\times 10^{-5}$	176-194° F
			104-140° F	Chars	Chars	Chars
			(Note 1)	(Note 1)	(Note 1)	Resistant
			(Note 2)	(Note 2)	(Note 2)	(Note 3)
			(Note 4)	(Note 4)	(Note 4)	Resistant
			Decomposes	Decomposes	Decomposes	Decomposes
			(Note 5)	(Note 5)	(Note 5)	(Note 5)

NOTE: Not all weak acids, weak alkalies, and organic solvents have like effect, and what is considered satisfactory resistance may vary. Chemical resistance should be considered a special problem.

1: No effect to slight decomposition dependent upon the acid.
2: Decomposed by oxidizing acids. No effect to slight effect on organic acids.

3: Resistant to all except strong oxidizing acids.

Table 14: Slight effect to marked effect dependent upon the alkali.

5: No effect to complete disintegration dependent upon the solvent.

*Manufacturers' data. Catalin Corporation

classified as such, "Haveg" 41, is substantially a cast phenolic resin filled with a special acid-washed asbestos. Unusually large pieces of chemical and other industrial equipment are made of "Haveg" by a process resembling the manufacture of concrete blocks, in which a putty-like mixture of resin and fibrous asbestos is loaded into inexpensive molds and allowed to cure without the application of pressure.

Pipe and fittings, valves, fume duct, cylindrical and rectangular tanks, covers, and accessories, towers, and special equipment of varied shapes are available in standard sizes. Special shapes can be manufactured without difficulty. Large vessels are usually re-inforced with metal bands or hoops, or wooden staves.

Cylindrical tanks up to nine feet in diameter and twelve feet in depth are manufactured of "Haveg," while tanks up to ninety feet in length can be made by bolting flanged sections together. Equipment of other shapes is available in comparable size.

"Haveg" 41 possesses excellent corrosion resistance and is particularly useful in chemical works. It is recommended for temperatures up to 265° F. It is resistant to most acids and salts, to chlorine, to the weaker bases, and to many solvents. It is attacked by hydrofluoric acid, oxidizing agents, and strong bases. Another grade of this plastic is manufactured with a carbonaceous filler which imparts resistance to hydrofluoric acid. A third quality has been developed for resistance to strong alkalies, as well as most acids. Nitric acid, sulfuric acid above 50 per cent, chromic acid, sodium hypochlorite, acetone, aniline, pyridine, bromine, and iodine should not be used in "Haveg" equipment.

Surface Coatings

Modified Phenolics. The adaptation of phenolic resins to surface coatings has taken place, for the most part, during the past twenty years. Their introduction was accelerated by the favor with which nitrocellulose lacquers were received after World War I, constituting a serious threat to drying oil varnishes of the older types. Phenolic resins made from phenol, itself, and formaldehyde are not soluble in drying oils. It has been found, however, that various natural resins such as the copals and especially rosin can be incorporated with the resin during preparation and the resulting product, constituting a chemical combination of phenol, formaldehyde, and natural resin acids, is then soluble in drying oils and, moreover, accelerates their drying. Similarly, fatty acids, especially those of drying oils, can be reacted with phenolic resins during their manufacture to yield products which are oil-soluble. Tung oil is commonly used as a modifier of this type. Modified phenolics of these two kinds, produced not only from phenol, but also from its homologs, are employed in the

formulation of interior 4-hour drying varnishes, in quick-drying primer coats for metals, in long-oil varnishes for exterior application, and in rubbing varnishes for wood furniture. They yield protective films of superior hardness and high gloss. They can be rubbed as quickly as dammar.

Unmodified Phenolics. It has also been found that several substituted phenols are capable of yielding resinous condensation products with formaldehyde which dissolve in drying oils to yield solutions which can

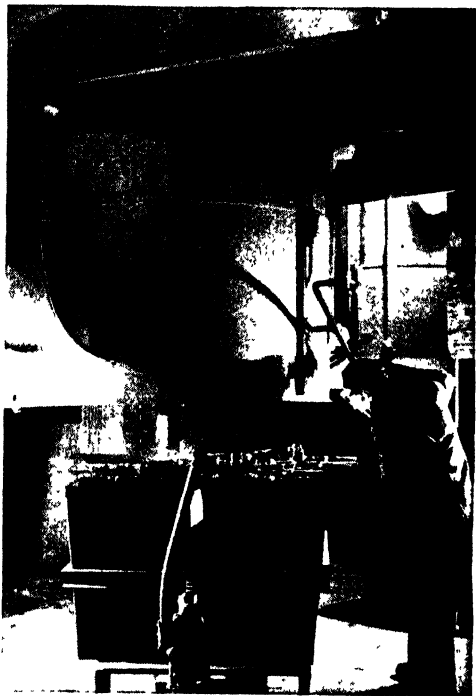


Figure 70. When a phenolic coating resin, such as "Amberol" F-77, has reached the desired reaction point in the kettle it is piped into batch cans. Upon cooling, the resin becomes a hard, translucent solid which is subsequently broken into small lumps.

Courtesy The Resinous Products & Chemical Co.

be diluted with petroleum thinners. This subject has already been mentioned in discussing the effect of structure of phenol upon resin formation. These unmodified oil-soluble phenolics, usually called 100 per cent or straight phenolics, are produced either by alkaline or acidic catalysts. In the former case, common catalysts are the hydroxides and sulfites of sodium, potassium, and ammonium; in the latter case, mineral acids, especially hydrochloric and sulfuric, are employed. Both base- and acid-catalyzed straight phenolics of the oil-soluble type appear to react with drying oils, the former more violently and with considerable foaming and liberation of gas. As would be expected, base-catalyzed straight phenolics cure, under the influence of heat, to C-stage insoluble coatings.

They are therefore used, sometimes in conjunction with such natural resins as rosin or copal, in the formulation of industrial baking enamels and chemical-resistant coatings.

Acid-catalyzed phenolic resins of the oil-soluble type are used in the formulation of air-drying varnishes, often in conjunction with other resins such as ester gum, cellulose acetate, and nitrocellulose. They improve gas-resistance, adhesion, resistance to water and certain chemicals, and exterior durability. Drying time is greatly reduced by incorporation of these resins in a drying oil, provided they are free of unreacted phenols which, on the contrary, behave as oxidation inhibitors and delay drying if present as such. Aging characteristics and water-resistance of straight phenolics are superior to those of modified phenolics. Acid-catalyzed straight phenolics are more flexible than base-catalyzed resins and hence yield more flexible coatings.

While modified phenolics are produced from phenol, cresols, and their homologs, the straight 100 per cent oil-soluble phenolics are made either from natural xylenols or from synthetic *p*-phenyl phenol, *ter*-butyl-, *ter*-amyl-, or *sec*-octyl-phenols, especially the para compounds which yield resins of much better heat-resistance and color stability than their isomers. While the xylenols are cheaper than the synthetic alkylated phenols, resins derived therefrom tend to discolor somewhat in the light. Hence, for some applications, xylene resins are undesirable, although coatings made from them are otherwise durable. Low molecular weight condensation products of acetone and phenol are also resinated with formaldehyde and used in formulating oil varnishes.

Other synthetic resins, especially alkyds and coumarones, are sometimes used in conjunction with phenolics in the formulation of protective coatings. They may be reacted with phenolics during the manufacturing process.

Oil-Free Lacquers. Heat-curing lacquers are also produced from soluble phenolics without the addition of drying oils, by the use of appropriate solvents, such as acetone or alcohols.

Phenolic lacquers of this kind are used for protective coatings on chemical equipment which is exposed to corrosive gases, on wooden fume stacks in the phosphoric acid industry, on metal parts exposed to hydrogen sulfide and sulfur dioxide (for example, the protective backing of locomotive headlight mirrors), on wood, aluminum, iron, steel, and paper parts used in the manufacture of rayon and other yarns. Such lacquers are invaluable in affording insulation and protection for electrical coils, armatures, and other windings. The thermoset resins not only possess good strength and insulating characteristics, but are also resistant to oil, in-

cluding transformer oils, and to both gasoline and water. Huge armatures of central power stations are impregnated with phenolic lacquers of this type, as are also those of generators and motors running down to less than $\frac{1}{4}$ hp.

Another important application of such resin solutions is in the manufacture of certain types of brake linings.

Lacquers of this kind can be applied by brushing, spraying, or dipping. The latter operation is used for coil impregnation, sometimes by a double-dip process in which the solvent-free but unbaked coating is given a second treatment. For the most thorough impregnation possible, vacuum operations are used.

Enamels. Phenolic enamels, usually possessing somewhat higher viscosity than so-called lacquers, but otherwise similar except for the presence of pigments, are used for analogous applications such as protective coatings on chemical plant equipment and backing for flood-light reflectors. A very important application is as impregnant for salvaging porous and sweating castings made of aluminum, brass, nickel and other metals.

Phenolic lacquers are usually baked at temperatures of 120 to 150°, baking time ranging from one to twenty-four hours, depending upon the job. The baking of impregnated coils, for example, requires a much longer period than the curing of an open coating.

Phenolic-Coated Cloth. Under the trade name "Revolite," thermosetting phenolic resin-coated fabric has been marketed during the past few years for many decorative and industrial applications. It is produced in a wide variety of colors. Its properties vary extensively, depending upon the kind of fabric used. Imitation leather finishes are available. It is characterized by excellent pliability. It resists alcohol, oils, soap and water, and the elements. It has been utilized in upholstery fabric, slip covers, drapes, and shower curtains. "Revolite" laundry roll covers fabricated from asbestos cloth, have received particularly favorable acceptance by commercial and institutional laundries which have used them to replace conventional cotton duck coverings. Multiple-ply "Revolite" has been adopted in various diaphragm applications, while suitably gummed fabric was used extensively during World War II to seal and simultaneously camouflage military planes and tanks shipped across both oceans.

Adhesives. Phenolic resins are used for a variety of adhesive applications both as self-hardening and heat-hardening cements. These cements are often produced by the consumers, but resins for adhesive applications are also available as highly viscous liquids or granular powders which

can be made up to a paste with a small amount of alcohol as solvent. Fillers such as asbestos and red lead are common, although addition of the latter causes rapid hardening.

Phenolic cements are used for such miscellaneous applications as the construction of resistors, commutators, transformers, lightning arresters, roof insulators, electric light bulb bases, and bases for radio tubes as well as for setting bristles. They are also very important in the manufacture of abrasive wheels, in which they are used to bond together the abrasive particles of emery or silicon carbide. Once set, these phenolic cements are resistant to steam, oil, chemical solvents and reagents, and heat.

Miscellaneous Products

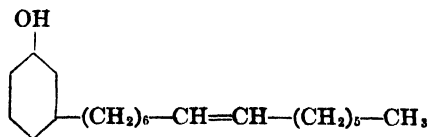
A development of the past few years which holds considerable promise for the future is the use of certain special resins, produced from polyhydric phenols or tannins, in water purification. Some materials of this category have been found to possess remarkable acid and base exchange characteristics, making practicable their use as organic analogues of the zeolites. Such products are available under the trade-mark, "Amberlite."

Among other miscellaneous applications of phenolics should be mentioned their utilization in the formulation of printing inks.

Foamed thermoset phenolics have been developed for insulating applications.

Cashew Nutshell Oil-Formaldehyde Resins

A novel development in phenolics during the past decade has been the introduction of a series of resinous materials based upon the oil derived from the outer shell of the cashew nut. This oil contains principally anacardic acid, $\text{HO} \cdot \text{C}_{21}\text{H}_{30}\text{CO}_2\text{H}$, and cardol, $\text{C}_{32}\text{H}_{52}\text{O}_4$. The raw material is poisonous to the skin, but, upon heating, anacardic acid is decomposed; the property of irritating the skin is lost; and the product is composed largely of a long-chain unsaturated phenol, cardanol, which has been assigned the formula:



Cardanol can be catalytically condensed with itself and also with formaldehyde. A wide range of commercial products is made by various combinations of these two treatments. They include "Oil Stop," a thick sirupy liquid capable of setting up by addition of paraformaldehyde and standing at room temperature. The product is a flexible, oil- and water-resistant gelatinous mass, somewhat resembling factice. "Oil Stop" is

used in cable splicing on the job, especially where reinforced with alternate layers of fabric. Lacquers, sold under the trade name "Harvel," are used in coating applications where unusual and corrosive conditions prevail. They have been particularly successful in equipment utilized in canning acid fruits and fruit juices, such as pineapple. Various products are sold under the trade name "Cardolite." Casting compositions and pulverulent cured materials are included among these substances; perhaps the most successful have been those used in brake linings and clutch facings where their excellent heat resistance has resulted in increased frictional characteristics and improved wear. Friction fortifying dusts, rubbery polymers, heat reactive liquid binders, and heat reactive molding powders are all utilized for these purposes, usually in conjunction with rubber and asbestos. Certain "Cardolites" have also been developed as compounding ingredients for rubber and synthetic rubbers, and as modifying agents in phenolic resin manufacture to improve impact strength.

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Chapter 7

Urea Plastics

History

The earliest remark concerning formation of an amorphous, insoluble material by reaction of urea with formaldehyde was recorded in the scientific literature in 1884 and occupied exactly one and one-half lines. The practical significance of this observation was not recognized for almost two score years. In 1918, a valuable discussion of the subject was contributed by the Englishman, A. E. Dixon, and during the following decade a series of developments in several countries finally resulted in commercial recognition of a new and important group of thermosetting plastics—the ureas.

The first patent in this field was granted to a Czechoslovakian, Hanns John, in 1920. Three years later, other patents issuing to the Viennese chemist, Fritz Pollak, served as the basis for commercial development of a transparent “organic glass” called “Pollopas.” This product, as it first appeared, was cast rather than molded and was produced in Vienna during the middle 'twenties. Similar materials were soon made in France and England under the trade names “Prystal” and “Plass,” respectively. This type of plastic was imported into the United States as “Luxite” and was later manufactured here for a brief period by the Luco Products Corporation of Brooklyn, under the name “Aldur.” Its surface hardness was far less than that of glass, although at one time journalistic enthusiasts glowingly predicted its use to satisfy general glazing requirements in hospitals, skyscrapers, and modern homes. The most serious objection to cast ureas was lack of weather resistance. Water absorption was high, a fact which, coupled with progressive condensation upon standing, caused loss of luster, cracking, and rapid failure of parts exposed to an atmosphere varying in humidity. Although the rather equable climate of the Continent appears to have permitted acceptance of transparent cast urea plastics abroad for a number of years, the more rigorous weather conditions of the United States speedily sealed their doom in this country.

In 1926, British developments led to the production of a molding powder by the combined use of urea and thiourea, the latter compound

improving both strength and water resistance. This product, available in a variety of colors, was manufactured by the Beetle Products Company of Oldbury, Worcestershire, and was in favor with British molders for several years. Patent rights in this country were acquired by the American Cyanamid Company and molding powders of thiourea plastics were put on the domestic market in 1929 under the trade-mark "Beetle." They were produced to the extent of some 200,000 pounds in 1930, but were relatively expensive to make, slow to cure, and hard upon the molder because the presence of sulfur caused corrosion of all but the most costly chromium-plated and stainless steel molds. Molded thiourea plastics were therefore also short-lived, although the trade-mark "Beetle" was preserved for application to future generations of urea plastics.

At about the same time that all these developments were occurring, a seemingly unrelated event transpired. In 1928, the Toledo Scales Co. established an Industrial Fellowship at Mellon Institute for the purpose of evolving a means of reducing the weight of their butcher's scale. This instrument was then housed in a heavy enamelled cast iron case which accounted for a considerable portion of its total weight of 165 pounds. Consumer demands dictated a decrease in weight and the logical place to begin with was the housing. This could, of course, best be accomplished by resorting to a lighter material. Use of a plastic was therefore indicated. The only moldable plastics available at that time were the phenolics, but their colors were limited to blacks and browns. For market research purposes, therefore, a number of experimental black enamelled scales were constructed and distributed to several retail meat merchants. Consumer tests established the fact that the fairer sex would refuse to purchase meat from butchers who used black scales—the color being taken as an indication of uncleanness. This psychological factor therefore ruled out the phenolics for scale housings and pointed to the desirability of developing a light colored plastic. In view of the interesting, though only partially successful results which had been achieved abroad in the field of urea and thiourea resins, an effort was made to develop a straight urea-formaldehyde molding powder. "Plaskon" was the ultimate successful outcome of this research. It was developed and placed upon the market for general use some time before scale housings were made of it, but the finished housing, subsequently molded by the Plastics Department of the General Electric Co., was much larger than moldings previously produced and set an imposing precedent for size.

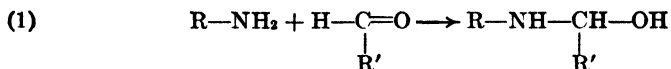
A few years later, a similar molding powder appeared on the American market under the trade name "Unyte." The producers of "Unyte" merged with the manufacturers of "Plaskon" in 1936. Other concerns have since entered the field. Meanwhile, the development of relatively

inexpensive synthetic urea from carbon dioxide and ammonia assured an adequate supply of essential intermediates for these resins.

During the decade which followed the initial commercial development of urea resins, other investigations led to their application as adhesives. In England, the Manchester firm of Tootal, Broadhurst, Lee and Co. pioneered their utilization as anti-creasing agents for cotton and rayon fabrics. Both of these applications are now important in the United States while, coincidentally, the use of urea resins in surface coatings has developed to significant proportions.

Chemistry

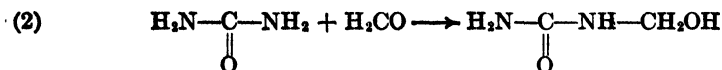
In general, the primary amino group in an organic compound is capable of reacting with various aldehydes to yield substances which range all the way from relatively simple addition or condensation products to complex resins. While the final materials obtained may be varied and involved, the initial reaction in every case, even though transitory, is presumably simple addition across the unsaturation of the carbonyl radical in the following sense:



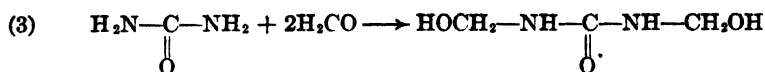
The ease of reaction (1) and the behavior of its products are determined in part by the nature of R and R' and in part by the conditions employed. In the production of commercial plastics, formaldehyde is used almost exclusively, although for highly specialized applications in resinous fire-retardent compositions recent developments point to the utility of acetaldehyde as well. Amino compounds utilized for industrial resins and plastics include urea, thiourea, melamine, aniline, *p*-toluene sulfonamide, and a few analogs of these compounds. Only urea will be discussed in detail in this chapter. As previously indicated, thiourea behaves in much the same manner as urea, save that resinous products are slower curing and corrode iron molds easily, so that its use has been largely abandoned except in laminating applications.

The reaction between urea and formaldehyde is contingent upon (1) the ratio of reactants, (2) the nature of the catalyst (especially pH of the reaction mixture), and (3) the temperature of reaction.

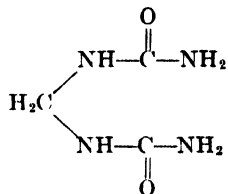
When one mole of urea is dissolved in water and reacted with less than one mole of formaldehyde under neutral or alkaline conditions and at room temperature, monomethylol urea is formed. If desired, it can be isolated from the reaction mixture as a crystalline compound.



If an excess of formaldehyde is employed, other conditions remaining the same, symmetrical dimethylol urea is produced and it, too, can be separated as a crystalline material if desired.

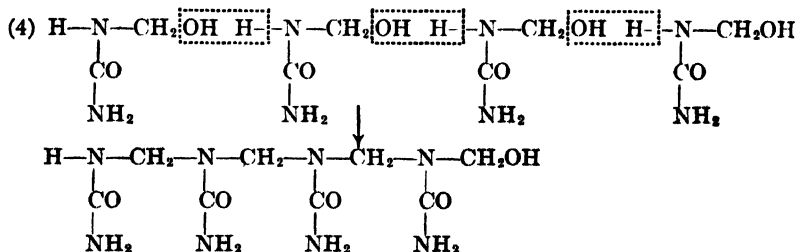


Under acid conditions, more complex reactions occur. Methylene diurea,

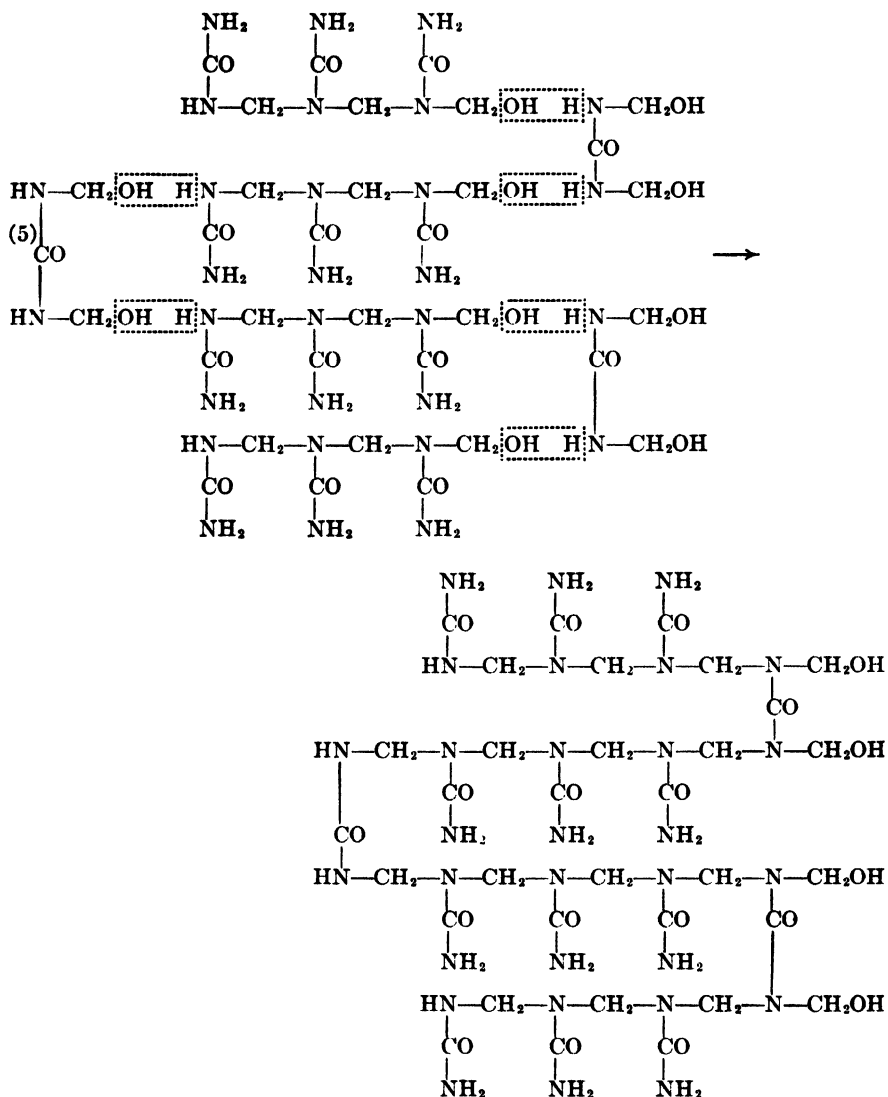


is formed as well as other amorphous, non-resinous polymeric methylene ureas. The constitution of the latter is as yet uncertain; their composition varies with the ratio of reactants. While it is probable that monomethylol urea is the first intermediate produced in acid solution, it cannot be isolated and reaction proceeds at once to the formation of these more complex condensation products. In the production of urea resins, therefore, the more readily controllable alkaline conditions are employed during initial phases of reaction.

Upon heating monomethylol urea or dimethylol urea under alkaline conditions, water-soluble condensation products are formed which, in complexity, correspond to B-stage phenolic resins, although they are more soluble. If now the solution is made slightly acid, with the pH adjusted between 4 and 6, a jelled insoluble resin is produced, especially under the influence of heat. Provided some dimethylol urea was originally present or is formed during the course of these treatments, an infusible, tridimensional, thermoset plastic results. Condensation of monomethylol urea proceeds in the following manner:

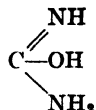


With dimethylol urea, cross-linking of several chains occurs, as for example:



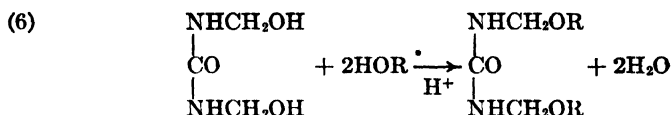
The molecular weight of the intermediate B-stage water-soluble condensation products averages about 400, corresponding to the reaction of some four molecules of urea with about eight molecules of formaldehyde. Conversion of these intermediate reaction products to C-stage resins under the influence of heat, an acidic catalyst, and pressure is the reaction which the custom molder carries out in transforming the molding compound into a finished shaped article.

The reactions which occur during resinification are in all probability more complex than those just outlined. Etheral linkages of the type $-\text{CH}_2-\text{O}-\text{CH}_2-$ are very likely formed to some extent, while a small amount of formaldehyde splits out during condensation. Reactions of urea are often very complicated because of its equilibrium with ammonium cyanate. A few authorities also believe that a tautomeric form of urea



enters into reaction with formaldehyde, although the experimental evidence is not convincing. However this may be, the principle reactions are those described above, for both mono- and dimethylol urea can be isolated from carefully controlled alkali-catalyzed reactions.

Dimethylol urea can react with alcohols under the catalytic influence of acids. The result is the formation of ethers or, more exactly, half formals, in accordance with the general reaction:



The products are soluble in alcoholic solution and condense further, like dimethylol urea itself, with elimination of ROH from two molecules of the half formal. Some R groups still remain after condensation, so that the B-stage products are soluble in organic solvents and can serve as components of surface coatings.

Molding Powders

Manufacture. In the production of urea resins, one mole of urea is first reacted with from 1.3 to 2.0 moles of formaldehyde in 40 per cent aqueous solution. This operation is carried out in the presence of a slightly alkaline catalyst, such as dilute sodium hydroxide or triethanolamine, and at a slightly elevated temperature (not over 50°). Because of the clarity of the finished resins, extreme cleanliness must be observed and condensation is best performed in nickel-clad or glass-lined reactors. A water-soluble product is thus formed and the aqueous solution is then cooled, filtered, and made slightly acid to a pH of 6 to 7. To the water-white solution thus obtained, α -cellulose is added, usually in the form of shredded sheets.

Addition of α -cellulose corresponds to incorporation of fillers in phenolic resins. It is used to the extent of 30 to 50 per cent of the total solids

content. The effect of adding α -cellulose to urea resins differs from the use of fillers with phenolics, however, in that microscopic examination of the end-product fails to reveal individual particles of cellulose physically admixed with resin. It is therefore commonly held that the cellulose is dispersed in the resin in a molecular state of subdivision, either by solid solution or, more likely, by actual chemical union, probably as a result of formation of cellulosic half-acetals. The B-stage resin admixed with α -cellulose is dried by removal of water *in vacuo* at temperatures of 60 to 80°, the final product having the appearance of popcorn which, indeed, it is often called. After drying, it is thoroughly ground with color pig-



Courtesy Bakelite Corp.

Figure 71. Charging a mixing unit with urea.

ments, mold lubricants, latent catalysts, and plasticizers. Inorganic pigments are ordinarily used as coloring materials, so as to ensure light stability. Metal stearates are commonly employed as lubricants.

Latent catalysts promote further condensation at elevated temperatures during molding. In the absence of moisture they are ineffective at room temperature. They may, however, become active even under atmospheric conditions in the presence of moisture, a fact which necessitates storage of urea molding powders in a cool, dry place. Typical latent catalysts include salts and esters which develop acidity upon heating, a result which may be dependent, in part, upon the presence or liberation of small amounts of moisture during molding. Dimethyl oxalate, hydrochlorides of organic amines, and sodium and barium salts of ethyl sulfuric acid are examples of such catalysts.

The principal plasticizers used are urea, thiourea, or substituted ureas. The purpose of these compounds is primarily to combine with unreacted formaldehyde and free methylol groups and to increase flow during molding. Excess hydroxyl groups which would impair water-resistance are thus eliminated and uniformity of cure is ensured. These results are important in order to minimize crazing and cracking which might subsequently occur because of continued condensation arising from inadequate cure of localized sections in the mold cavity. Plasticizers also impart limited flexibility

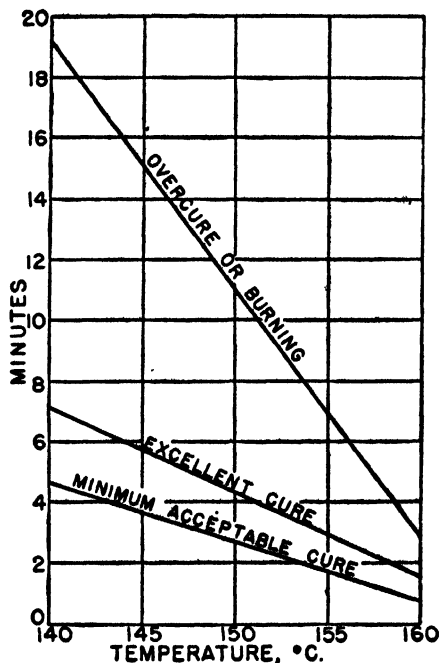


Figure 72. Curing time for 0.070 inch thick specimens of "Plaskon," medium molding compound.

Courtesy Plaskon Division, L.-O.-F. Glass Co.²⁴

to the hot-molded pieces, although they have little or no effect at room temperature.

After thorough mixing, the molding compound is packed for shipment in the form of fine powder of the consistency of flour; or it is compressed and granulated before packaging, to reduce its bulk factor.

Molding Conditions. The molding of urea-formaldehyde plastics takes place under more restricted conditions than that of their analogs, the phenolics. Temperatures are held between 270° and 320° F and pressures range between 3000 and 9000 lbs/sq in. Molding time varies from ½ to 10 minutes, depending upon size and shape. Molding conditions for 0.07 inch thick "Plaskon" pieces are shown in Figure 72.

Conditions yielding good results with a variety of typical "Plaskon" moldings are listed in Table 13.

Table 13. Conditions Producing Good Results on Representative "Plaskon" Moldings*

Name of Piece	Projected Area (square in.)	Depth (inches)	Thickness (inches)	Pressure (tons per cavity)	Steam Pressure (lba)	Approximate Mold Temperature ($^{\circ}$ F)	Cure Time (minutes)	Approximate Number of Cycles per Hour
Bowl	28	3	0.035	40	80	300	3	15
Biscuit Cutter	4	1	0.030	12	80	305	2	20
Buttons	1	0.062	0.062	1	90	315	1½	30
Lamp Shade	39	5	0.045	75	70	—	3	—
Lamp Shade	94	3	0.050	200	75	—	3	12
Box-Circular	16	3	0.035	30	70	—	3	—
Box-Lid	17	½	0.075	30	70	—	3	—
Scale Cabinet	64	8	0.125	300	60	295	6	7
Radio Housing	95	7	0.156	330	85 (with cooling cycle)	—	5	5
Tumbler	7	3¾	0.050	20	75	300	4	10
Electrical Cube Tap	1½	¾	0.070	3	100	315	½	40

As with the phenolics, inserts can be molded into urea plastics without difficulty, provided ample thickness of molded material be allowed around the insert to prevent cracking.

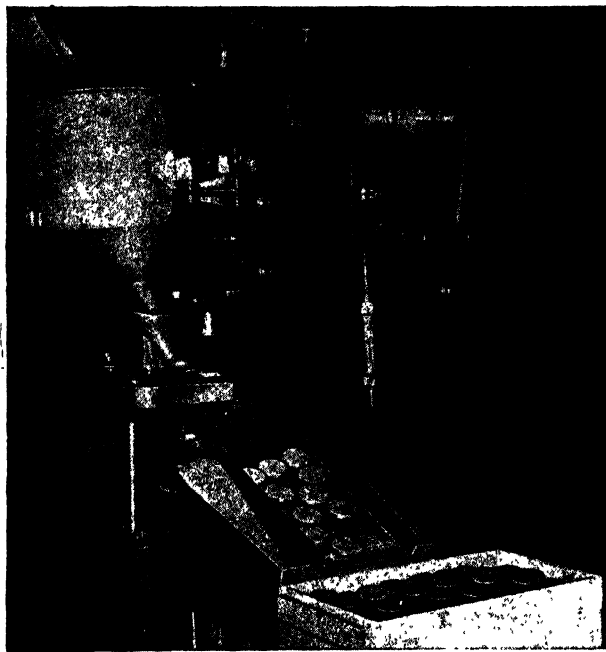
Urea molding powders are manufactured in several degrees of plasticity—from hard to extra soft. Special long flowing grades are available for complicated moldings and large articles of deep draw. Best moldings are obtained with semi-positive, semi-automatic molds in which pressure is applied continuously throughout the cycle and in which a seal is maintained on the mold cavity. Cross-sectional thicknesses in excess of $\frac{1}{4}$ inch should be avoided.

Preforming and tableting are commonly practiced.

Properties. The outstanding property of molded urea plastics is their light color. The resins themselves are transparent. The natural color of α -cellulose filled ureas is a translucent milky white that can be easily converted to a pure solid white by addition of titanium dioxide, or to numerous permanent pastel shades and brilliant solid colors by addition of other stable pigments. Unlike many other plastics, ureas do not lose luster by handling; on the contrary, their polish improves.

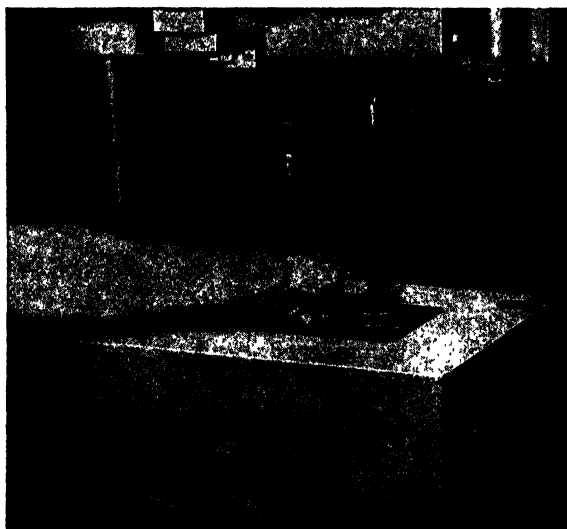
Ureas are less resistant to water than the phenolics and should never be used in contact with hot water. When well-cured, however, they are sufficiently resistant to water at room temperature to permit application in bathroom fixtures and "unbreakable" tumblers. In these applications, of course, extreme dimensional stability is not essential and contact with water is not sufficiently long to permit saturation of the plastic. Continued exposure of urea-formaldehyde plastics to an atmosphere of widely fluctuating humidity will often give rise to cracks as a result of alternate absorption and loss of water. This behavior, common to the early ureas, has now been greatly improved. The water absorption of urea plastics is, in part, a function of the number of free $>NH$ and $-CH_2OH$ groups remaining uncombined in the finished product. Both of these radicals, especially the latter, are hydrophilic and tend to absorb water. The best plastics are therefore those in which manufacturing and molding conditions are adjusted to reduce these groups to a minimum. Under-cure, caused either by too low temperature or too short time of molding is reflected in poor water resistance. Chalking or whitening of the surface will occur if undercured ureas are boiled in water for ten or fifteen minutes. Surface cracks may develop in improperly cured test pieces which are dried rapidly after boiling. More meaningful breakdown tests are sometimes applied to urea moldings by exposing the shaped articles to a cycle of an alternate dry, then saturated atmosphere at a temperature of $100^\circ F$: A 24-hour period is allowed under each set of conditions.

Urea plastics are not resistant to either weak or strong acids, nor to



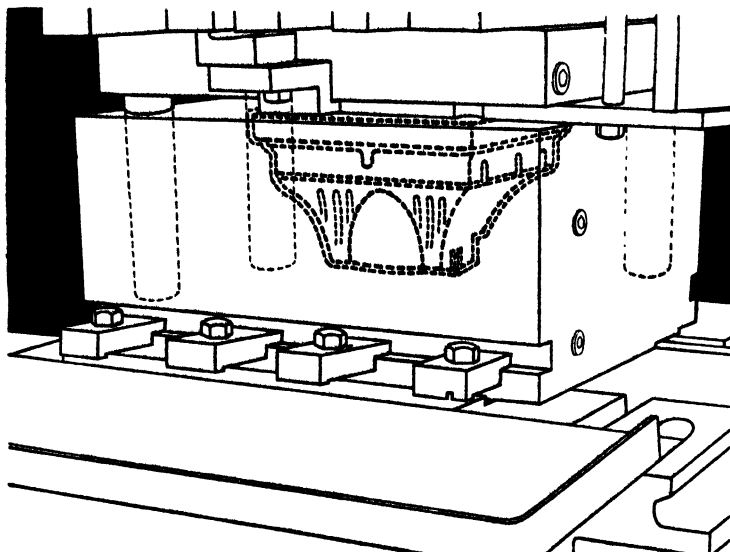
Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 73. Compressing urea-formaldehyde molding powder into pills for convenient handling.



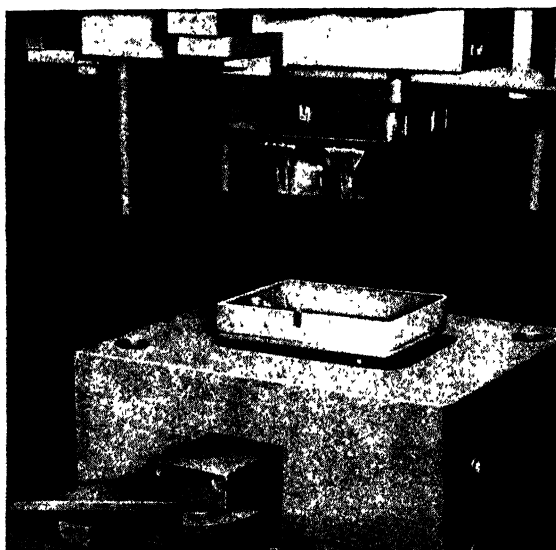
Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 74. Loading "Plaskon" pills into heated steel forming mold.



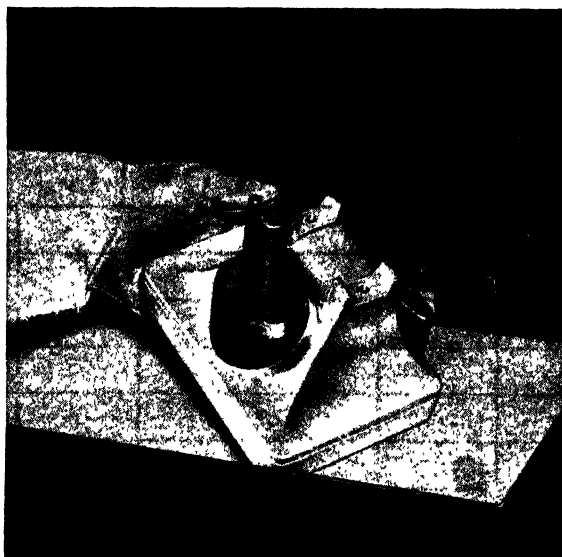
Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 75. Phantom view showing mold closed and dies in molding position.



Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 76. Press opened. Molded urea article partly ejected from die.



Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 77. Molded article and loose parts of mold removed

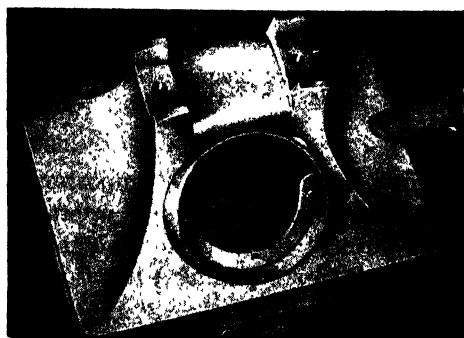


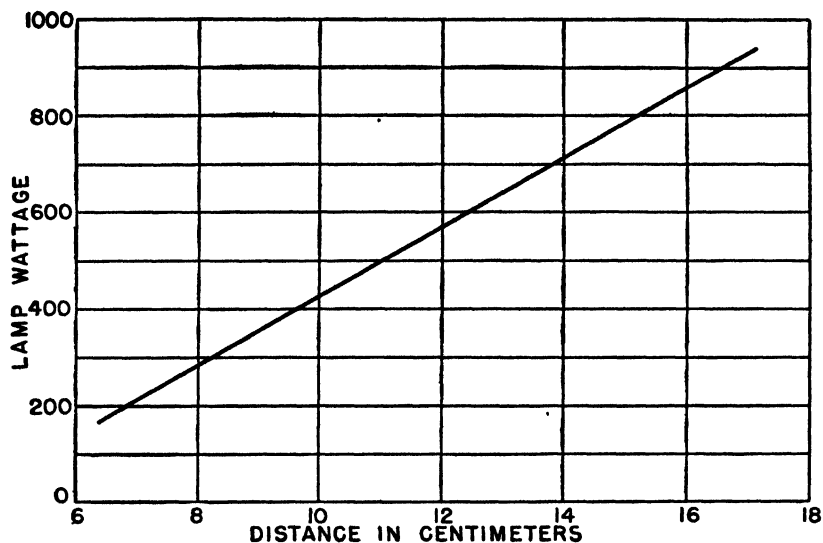
Figure 78. Finished molded "Plaskon" article

*Courtesy Plaskon Division,
L.-O.-F. Glass Co.*

strong alkalis. On the other hand they show good resistance to weak alkalis and are unaffected by organic solvents, including grease and oils. They possess neither taste nor odor.

In order to avoid thermal decomposition with attendant opacification, urea-formaldehyde plastics should not be called upon to operate continuously above 170° F. Temporary use at temperatures up to 240° F will not injure them, however, if such exposure is brief. Unlike phenolics, heat-resistant ureas cannot be compounded by adding inorganic fillers because

the unique effect of α -cellulose is essential to proper strength characteristics and good moldability. The upper operating temperature limit of urea-formaldehyde plastics is of particular importance in illuminating applications where it dictates permissible distances from lamp bulb to reflector, as shown in Figure 79.



Courtesy Plaskon Division, L.-O.-F. Glass Co.²³

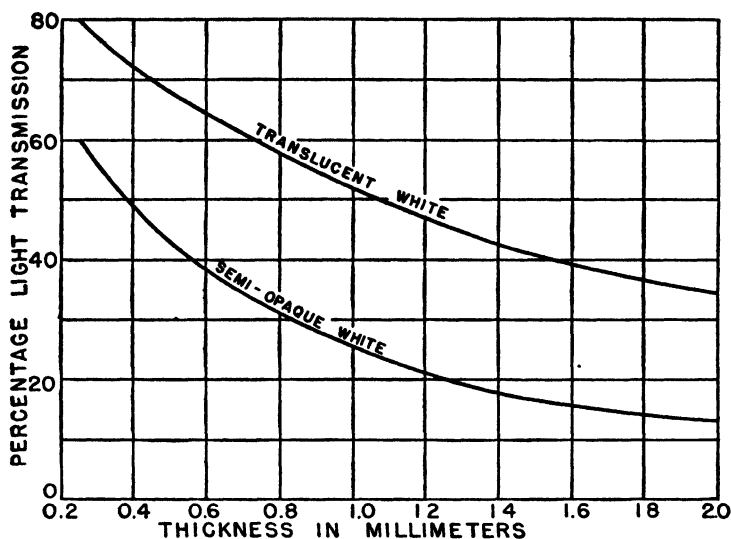
Figure 79. Relation between wattage and distance of lamp filament from "Plaskon" reflector surface in semi-indirect luminaries for safe operating temperature of 165° F.

The translucence of urea-formaldehyde plastics is of great importance to illuminating applications. Unpigmented plastic transmits approximately 65 per cent of the incident light through sheets 0.040 inch thick. Transmissivity can be varied from this figure to zero, being a function of pigmentation and thickness. The total light efficiency:

$$\frac{\text{reflected light} + \text{transmitted light}}{\text{incident light}}$$

of white urea plastics in thin plates averages about 90 per cent. The relationship between light transmission and thickness for two standard illuminating materials is shown in Figure 80.

Upon passage of an electric arc across their surface, urea-formaldehyde plastics do not carbonize. Unlike the phenolics, therefore, no conducting carbon path is formed between electrodes and the ureas can be utilized where arc resistance is of importance.



Courtesy Plaskon Division, L.-O.-F. Glass Co.²³

Figure 80. Light transmission of "Plaskon."

The principal properties of urea-formaldehyde plastics are represented by those of "Plaskon" tabulated in Table 14.

Among molded plastics, ureas exhibit unusual surface hardness. Machinability is poor and is not recommended except for simple drilling and tapping operations.

Applications. The brilliance, variety, and lightness of colors available in urea plastics, coupled with good molding qualities and other favorable characteristics have brought them into high favor for the manufacture of a multitude of articles including buttons, buckles, knobs, piano keys, watch boxes, handles on ranges and refrigerators, instrument dials, housings for radios, scales, meat grinders, clocks, thermostats, and sales recorders. Resistance to mild alkalis permits their use in bathroom fixtures and tumblers. Lack of taste and odor, and resistance to grease and oils, have adapted them to the manufacture of shatter-proof dishes. Although the term "non-breakable" is somewhat of an exaggeration, these articles can stand much greater abuse than china or glass. At first placed on the market primarily for picnic ware, urea dishes are now invaluable aboard ships, both merchant and naval, and proved a godsend in public kitchens established in blitzed areas of England during the early days of World War II.

Grease, oil, and chemical resistance are also determining factors in the use of urea plastics for bottle closures and cosmetic containers, especially for salves and creams, and for molded tablet dispenser housings.

Table 14. Physical Properties of Molded "Plaskon" ^{23, 24}

Property	Value
Specific Gravity	1.48-1.50
Weight per Cubic Inch	0.85-.91 oz, 24-25 grms
Tensile Strength	8,000-13,000 lbs per sq in
Compressive Strength	25,000-35,000 lbs per sq in
Modulus of Elasticity	1,550,000-1,655,000 lbs per sq in
Impact Strength	
Charpy, Unnotched $\frac{1}{2}$ " \times $\frac{1}{2}$ " bar	0.7-1.2 ft lbs
Distortion Under Heat	
5 $\frac{1}{2}$ lb load	7 mils or less at 127°
Flexural Strength	10,000-14,000 lbs per sq in
Dielectric Constant	
60 cycles	7
10 ³ cycles	6.4
10 ⁶ cycles	6.3
Dielectric Strength	600 volts per mil
Volume Resistivity	2 to 2.8×10^{13} ohm-cm units
Surface Resistivity	2 to 2.2×10^{13} ohm-cm units
Power Factor	
60 cycles	0.039 (3.9%)
10 ⁶ cycles	0.032 (3.2%)
Hardness	
Brinnell	
500 kilos 10 mm ball	48-54
Scleroscope	80-95
Firth Hardometer	1.14 mm (equivalent to 46 Brinnell)
Mohs Scale	3-3.5
Heat Resistance	
Continuous Exposure	75°
Intermittent Exposure	120°

Because of their unique combination of color, controllable translucency, high light efficiency, and relatively good heat stability, urea-formaldehyde plastics have made for themselves a well-deserved place in the fabrication of electric light shades and reflectors for both filament-type bulbs and fluorescent lamps. I.E.S. portable lamp diffusers, reflector bowls for commercial lighting, various types of lenses and shades for transparent lighting, and numerous types of decorative lamps are now made of urea resins. Light weight, as well as impact resistance, gives these materials an advantage over glass and other ceramics. Light reflectors have been marketed up to 28 inches in diameter.

Resistance to tracking and arcing, coupled with relatively high dielectric strength, adapts the ureas to fabrication of switches, circuit breakers, fuse blocks, switchboard parts, line connectors, plugs, and color-coded electric switches for ordinary services as well as in connection with high voltages, high frequencies, and insulators which are continually subjected to voltage flash-over.

Urea molding powders are produced by several companies and sold

under such trade-marks as "Bakelite" urea, "Beetle," "Plaskon," and "Sylplast."

Prices averaged about 32 cents per pound in 1945.

Of the 48,000,000 pounds of urea resins produced in the United States during 1944, approximately 19,000,000 pounds went into the manufacture of molding compounds.

Laminated Products

Urea resins find considerable application in the production of laminated plastics which can be machined in the same way as other laminates. In the discussion of phenolics, it was pointed out that relatively slow curing cresylic acid resins were employed for laminating purposes. For the same reason, it has been found that slower curing condensation products of formaldehyde with mixtures of urea and thiourea are preferable to straight ureas for this application.

The process employed is substantially the same as in the production of other laminated goods, save that an aqueous solution of the urea-thiourea resin is used and fillers are generally confined to the best grades of rag or alpha paper and cloth. The impregnated sheet material is dried at 190° to 230° F and is then ready for lamination, the resin content varying from 45 to 65 per cent. The higher figure is usually attained by double treatment of the paper and is normally employed for surface sheets to increase weather resistance.

Urea resins are used in producing light-colored laminates in which the surface sheet is impregnated therewith, while the body of the plastic may be *either* urea *or* phenolic. As in the case of molded ureas, laminates comprising at least a surface sheet impregnated with urea resin can be produced in all colors, including whites and pastels, by suitable selection of light-stable pigments. The paper of the surface layer may be colored or printed, before impregnation, in any appropriate design such as wood, marble, or cloth. Matte or grained surfaces are produced by molding between engraved plates. Satin finishes are obtained by frictioning the cured stock with pumice or other fine abrasive. The use of cut-out designs in vari-colored paper or other materials, such as metals, permits wide flexibility in the use of inlays, both on the surface and beneath.

Decorative laminates, usually based on phenolics with light urea surfaces and often backed by plywood, find wide utility as table tops in restaurants, cafés, and bars and in lounge and dining cars of modern trains, in counter tops of stores, in wall and door panels of office buildings and theatre lobbies, in refrigerator door panels, inlaid mural designs, name plates, instrument panels, and instruction charts. The last three applications have assumed particular importance in military equipment.

If all of the laminations are of a high quality paper base and if urea resin is used to impregnate them all, then the finished product is translucent and can be used for numerous applications whose potentialities have not yet been fully recognized. Translucent laminates $\frac{1}{8}$ inch thick will transmit approximately 48 per cent of the incident light. Both in natural and pigmented white, these materials are used for lamp shades and illuminating panels. If supported mechanically, they can be made to hold slight bends, while if they are thin enough, they can even be given a permanent simple curvature by heating to a temperature between 250° and 300° F. This permanent set can be imparted upon heating in spite of the fact that the ureas are thermosetting.

Translucent laminates are available in many shades. Colored or printed designs upon one of the sheets can be made plainly visible by assembling it as the next-to-surface layer. In this manner, it can not only be seen readily, but it is protected from wear by the top sheet.

Opaque surface layers are often combined with translucent cores in white or other contrasting colors. The composite laminate can be sand-blasted or engraved with a pantograph or other instrument. This type of construction is now extensively used in making name plates and instruction panels which can be illuminated from the back if the rear surface is clear.

Translucent urea laminates are now common in the fields of illumination, display, and decoration. Vending machines and "juke boxes" make frequent use of colored sheets, often shaped. Dials, especially for radios, fluorescent lighting fixtures, illuminated signs and markers are increasingly fabricated from these laminates. By incorporation of suitable pigments, both organic and inorganic, during manufacture of the laminate, these products can be made either fluorescent or phosphorescent. Fluorescent instrument panels have become essential parts of many military planes.

Low-Pressure Molding-Laminating

Like the phenolics, urea resins can be used to impregnate either cloth or paper which can be wrapped into complicated shapes and large sizes over inexpensive forms built of wood, concrete, etc. They can then be cured by application of heat under low-pressure—from 250 lbs/sq in to 15 lbs/sq in. Although strength characteristics of this type of low-pressure molded-laminated material are less than the optimum, and although water absorption is higher than with products molded under high pressure, the advantages to be gained by ease of fabrication, elimination of expensive molds, and practicability of forming large shapes augur well for the future of this wartime development.

Adhesives

The growth of urea adhesives during the past five years has been spectacular. Even before the outbreak of World War II, they were being produced in Germany at the rate of 200,000 pounds a month for use in military aircraft. Substantially the same reactions are carried out in their manufacture as have already been described in connection with molding powder. Urea-formaldehyde adhesives are sold both in solution and as dry powders. In the latter case, water is evaporated from the intermediate B-stage resin. The dried product is capable of being admixed with water



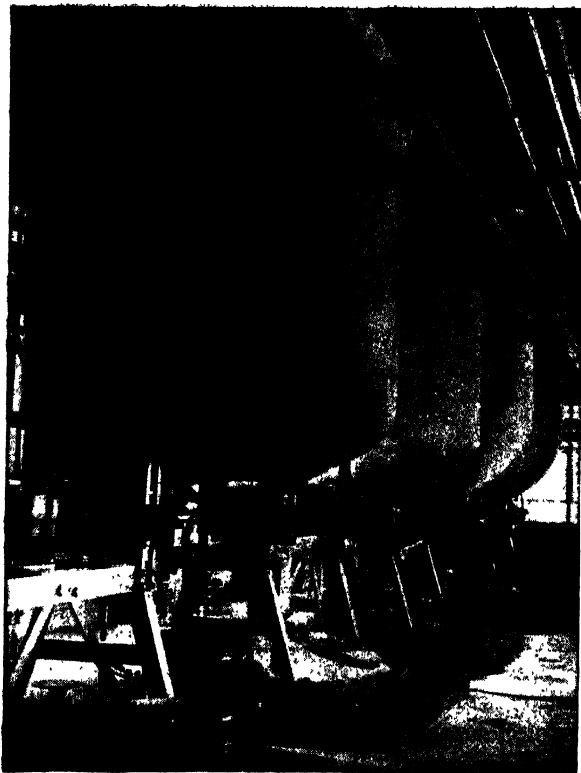
Figure 81. The production of urea-formaldehyde resins requires precise control if the viscosity and properties of the resin are to be kept within narrow limits of variation.

Courtesy The Resinous Products & Chemical Co.

to yield a solution which, upon addition of an acidic catalyst, will cure to a tridimensional water-resistant film. In part because of the polar nature of the resultant resin, it possesses excellent adhesion to polar or hydrophilic surfaces. At the same time, its tridimensional character makes it far more water resistant than such adhesives as fish glue. Urea resin adhesives are often mixed with finely divided wood flour which is used for the same reasons as α -cellulose in molding compounds. They may be extended with rye or wheat flour or with blood albumin in order to decrease cost. Their adhesive strength is diminished by these extenders, although not directly in proportion to the amount added. Even when considerably extended, they are much superior to older types of glues in strength, water-resistance, and anti-rotting properties. Thick wood-flour filled putties can also be prepared by using these adhesives as binders.

Both cold-setting and hot-setting glues are manufactured. The former are cured at room temperature by addition of an acidic catalyst, such as

ammonium chloride, to the aqueous solution. Hot-set glues require heat for effective cure because of the use of a less active catalyst. Dry glues are on the market which contain resin and hardener mixed, requiring only addition of water to make them active. After being mixed with water, such glues are serviceable for only a short period, usually from one to



Courtesy The Resinous Products & Chemical Co.

Figure 82. The "Uformites" are manufactured in this battery of kettles where urea and formaldehyde are reacted together under controlled temperature and pressure. During the reaction, samples are taken at frequent intervals for control laboratory evaluation.

four hours, depending upon the temperature. Copper equipment should be avoided in mixing; iron, enamel, and glass are satisfactory.

In using cold-setting urea glues, coated surfaces should be joined within fifteen minutes from the time of application of the adhesive. Bonding pressures usually range from 100 to 250 pounds per square inch and should be maintained from 2 to 24 hours, depending upon the temperature. The resin continues to cure for a week, but at room temperature pressure

may be relieved in less than 24 hours, ordinarily in about 8 hours. Urea-formaldehyde glues have been widely used in plywood manufacture for both marine and aircraft structures, and in assembly of assault boats and other important military equipment. Unlike phenolic adhesives, ureas do not require careful humidity control of the veneers to be bonded, up to 15 per cent moisture being permissible without special treatment before or after glueing. They are invaluable in the manufacture and repair of



Figure 83. In this five-story tower, liquid resin is sprayed as a fine mist where heated air converts it to a powder. The spray drying process is used for phenol-formaldehyde and urea-formaldehyde resins for plywood adhesive and paper treatment. By spraying it is possible to control the stability of the resin and to cut shipping weight by elimination of solvent.

Courtesy The Resinous Products & Chemical Co.

furniture and are recommended for bonding linoleum. They possess no merit for metal joining.

Because these glues are not subject to bacterial action, glue lines do not rot. Fine wood veneers may be bonded with urea adhesives because they are non-bleeding. Dyed wood should be investigated prior to bonding to ascertain the effect of the dye on the adhesive. If it affects pH, the latter may not cure.

Urea-formaldehyde adhesives are marketed under such trade names as "Plaskon" cold-set and hot-set glues, "Uformite," and "Weldwood Waterproof Glue." Price in 1944 was about 22 cents per pound in bulk. During that year, about 22,000,000 pounds of urea adhesives were manufactured.

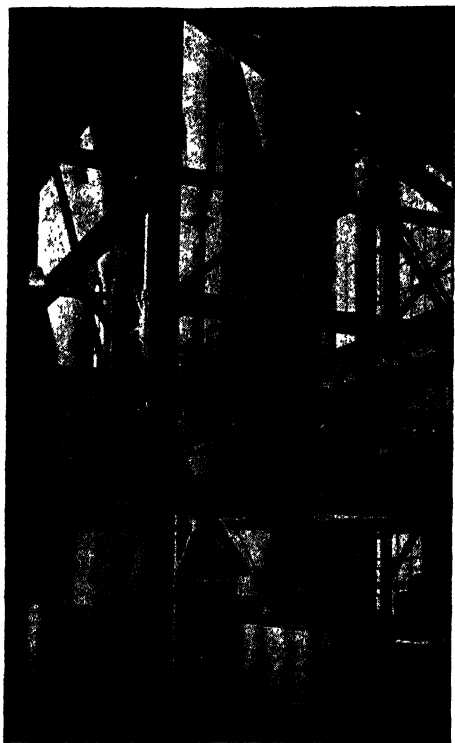


Figure 84. After urea-formaldehyde resin has been converted to a fine powder in the spray drier tower, it is collected in the large cones shown at the top. Fed through conveyor ducts, the powdered adhesive is then screened and packed for shipment.

*Courtesy The Resinous Products
& Chemical Co.*

Surface Coatings

The versatility of the ureas has increased in a phenomenal manner during the brief period of their commercial development. They are now indispensable in light-colored lacquers, especially whites where light-stability is an important element.

Upon treatment of dimethylol urea with an alcohol in the presence of an acidic catalyst, a half-acetal is formed which is capable of undergoing further condensation with elimination of alcohol and ultimate formation of a thermoset resin. Polyhydric alcohols, especially ethylene glycol, behave similarly and give rise to products which retain stability in solution even after long standing. These half-acetals, specifically formals, are soluble in alcohols and the solutions can be diluted with such hydrocarbon solvents as benzene, xylene, or hydrogenated naphthas like the "Solvessos." By addition of suitable pigments and application of the resultant lacquer to metal or other surfaces, followed by baking at temperatures of 225 to 325° F, using either oven heat or infra-red, surface coatings are produced which possess excellent light stability and good surface hardness. The

principal objection to such coatings is lack of adhesion. This fault is magnified by hardness and brittleness which tend to make these coatings chip. To avoid such difficulties, therefore, urea resins for surface finishes are not used straight, but are always admixed with oil- or phenol-modified alkyd resins, often in the ratio of 1:1. Because of the alcoholic nature of a portion of the alkyd structure, it is probable that the final resin embodies an actual chemical union of the two types—urea and alkyd—established by half-acetal linkages between them. Ureas are also frequently admixed with certain other resinous materials besides the alkyd in surface coating formulations, notably ethyl cellulose, nitrocellulose, and the natural resins.

These coating materials are now of vast importance in surfacing kitchen ware, bathroom fixtures, hospital equipment, and refrigerators as well as other articles which must be finished in light shades that will not discolor over long periods and that will be relatively immune to soap, oils, solvents, and other chemicals. For such finishes, ureas are usually admixed with alkyds modified with saturated fatty oils or their corresponding acids. Mixed with alkyds modified with drying oils or drying oil acids, urea resins now provide important lacquers for trucks and automobile bodies, bicycles, toys, and automotive accessories where rough usage or exterior weathering will be encountered. To provide greater water-resistance for washing machines and other laundry equipment, as well as for automotive primer coats, ureas are frequently used in combination with phenol-modified alkyds.

The coating of textiles and leather, as well as floor tile, with mixed urea-alkyd resins is being increasingly practiced. Resistance to mustard gas is imparted to textiles by application of flexible urea-alkyd coatings.

Urea resins for coatings are manufactured under such trade names as "Bakelite" urea, "Beckamine," "Plaskon," "Rezyl," and "Uformite."

Miscellaneous Applications

By treatment of cotton, rayon, and velours with aqueous solutions of low-molecular weight condensation products of urea and formaldehyde, followed by heating to temperatures sufficiently high to cure the resins, crease- and crush-resistance as well as some degree of water-repellence, are imparted to the fabrics. Color is not affected because the resins themselves, like other forms of the ureas, are colorless. Finishing of textiles in this manner has met with much favor because the necessity for ironing after derangement is obviated. Crease-proofing with urea resins is safely applicable to colored goods, but caution should be exercised in its use with colorless textiles which may be subsequently bleached; chlorine may give rise to chloramine which, under a hot iron, may tender the fabric.

Urea-formaldehyde textile treating agents are sold under such trade names as "Onyx" NCF and "RHonite."

More highly condensed urea-formaldehyde resins, such as "Onyx" liquid resin SS, may be used to impart special effects to textiles.

Urea resins have also been adapted for use in printing inks for textiles and in high-speed lithographic printing inks.

Various urea resins are being developed as weather-proofing and fire-retarding coatings for application to paper, wood, and textiles, especially duck. Some of the fire-resisting properties of these resins can be traced to the evolution of an extinguishing film of nitrogen gas liberated upon combustion of the resin. Condensation products of urea with mixtures of formaldehyde and acetaldehyde offer particular promise in this field.

Urea resins are employed in aqueous solution as a paper size to improve wet strength. This use is particularly important in the manufacture of paper hand towels and paper cartons.

Surface active agents can be dissolved in aqueous solutions of urea-formaldehyde resins which are then whipped into a foam and set. Subsequent elimination of water leaves a porous structure, extremely light in weight and of excellent heat insulating value. Such products have been made in Germany for several years under the name "Igelite" and are currently being developed in this country. Foamed "Plaskon" has an apparent density of 0.83 lbs/cu ft. Its heat conductivity is 0.23 B.t.u./sq ft/hr/° F/in. One of its most interesting characteristics is unique sound-proofing value.

Sharples Chemicals, Inc., is developing several resins from various substituted ureas, including water-soluble types from ethyl and ethanol urea ("Hydramine") and hydrocarbon-soluble types from *n*-butyl urea ("Buramine") and *uns*-dibutyl urea ("Plastamine").

An interesting discovery of great potential importance was recently made at the U. S. Forest Products Laboratory. If wood, such as oak, is soaked in a hot aqueous solution of urea, it is plasticized thereby and, while still hot, can be bent and twisted into odd shapes which retain their form after being cooled in position. Upon reheating, such treated wood again becomes plastic and returns to its original condition. If now, urea is replaced by water-soluble urea formaldehyde condensation products, the same plasticizing action is exhibited. Once the wood is impregnated with resin, the latter can be cured and whatever shape has been given during soaking is permanent.

This discovery has formed the basis for the development of "transmuted wood." Methylol urea is utilized in aqueous solution as the impregnant for any desired species of wood. The solution is conveniently prepared by dissolving in water appropriate amounts of urea and dimethylol urea

(DMU), both of which are available commercially in solid form. Wood acids serve as condensation catalysts and effect polymerization of the methylol urea *in situ*. Heat accelerates curing. Pressure may be applied to yield products of varying degrees of density and depth of hardness, depending upon conditions. Polished or embossed surfaces may be imparted to the transmuted wood by compressing between platens of appropriate style. Swelling, shrinking, warpage, hardness, and strength characteristics, as well as appearance may all be improved by this sort of treatment.

During 1944, approximately 3,500,000 pounds of urea resins were produced for textile, paper, and leather treatment and a similar amount was manufactured for other miscellaneous uses.

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Chapter 8

Melamine Plastics

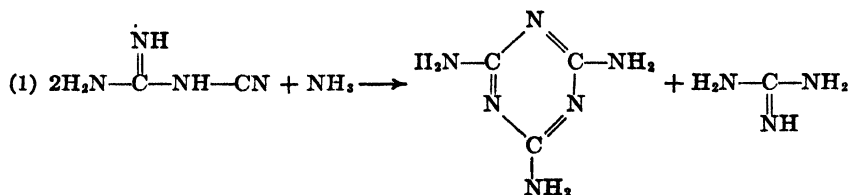
History

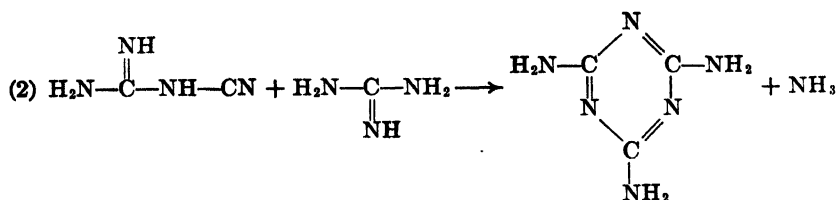
Melamine, the essential intermediate for the melamine plastics, has been known for more than a century. It was produced by Liebig in 1834, but only recently have methods been developed for its industrial manufacture. It first appeared on the American market in 1939. For a year or two prior to that time resins derived from it had been made in Europe—first in Switzerland, then in Germany. As with the ureas, the earliest Continental melamine plastics were used without fillers and were water-white. Transparent melamine resins, however, have never been sold in the United States, experience acquired with other plastics having indicated their probable failure because of climatic conditions.

The first melamine resins (often called melamines, for short) produced in this country were made by the American Cyanamid Company and were sold for laminating purposes. They are also now available for molding, surface coating, and other applications. The patent situation became surprisingly complicated in 1941 by issuance of the basic patent for their manufacture to the Monsanto Chemical Company. Both Ciba and Cyanamid own important subsidiary patents and have reached agreements with Monsanto whereby they are allowed to operate under the controlling one.

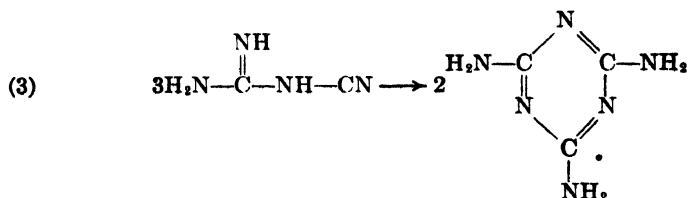
Chemistry

The tardiness with which melamine resins appeared upon the market was largely the result of inadequate methods for the preparation of melamine itself. During the past decade, it was found that this heterocyclic nitrogen compound, otherwise known as triaminotriazine, can be obtained in good yields by heating dicyandiamide with an anhydrous alcoholic solution of ammonia in an autoclave. The intermediate reactions which appear to occur are as follows:

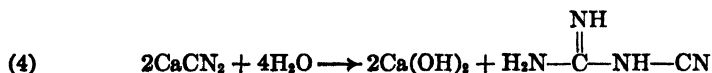




The overall reaction is therefore:



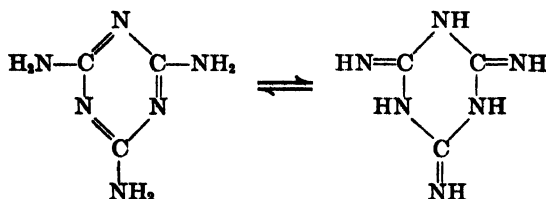
Dicyandiamide is obtained industrially from calcium cyanamide by reaction with boiling water or hot dilute sulfuric acid:



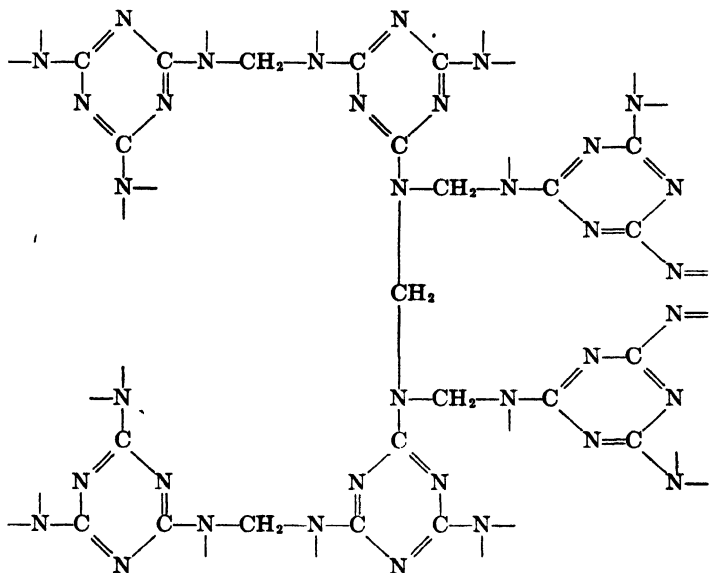
Calcium cyanamide, in turn, is derived from calcium carbide by passage of nitrogen through hot calcium carbide admixed with about 10 per cent of calcium chloride which facilitates absorption of the gas.

The reactions involved in the formation of melamine resins are similar to those employed in the production of their counterparts, the ureas.

Melamine exists in two tautomeric forms:



Possibly because of this fact, it differs from urea in that all six hydrogen atoms can be replaced by methylol groups upon reaction with formaldehyde. Despite this reactivity, however, only three methylol groups, or less, are introduced for the production of insoluble, infusible resins. Assuming that the tautomeric form possessing primary amino groups enters into reaction, a small portion of a molecule of melamine resin may be represented as follows:



Like the ureas, the intermediate methylol derivatives of melamine can be converted into half acetals by reaction with alcohols in an acidic medium. The resultant products are soluble in organic solvents and are used as components of surface coatings, always in combination with alkyds. They are also employed in textile treating agents for stabilizing woolsens.

Molding Powders

Melamine molding powders are produced much like their counterparts, the ureas, save that the final condensation need not be carried out with as low a pH. During the molding operation, curing will occur without acidic conditions so that these materials may sometimes be combined with slightly alkaline fillers or with other resins, such as the phenolics, which set up under alkaline conditions.

The pure resins are colorless. Molding powders can therefore be produced in light, pastel shades. These plastics are also odorless and tasteless. They possess considerably greater resistance to heat and water than is exhibited by the ureas. In the last two respects they more nearly resemble phenolics. Moreover, they are not dependent upon the use of α -cellulose as a filler. Although, indeed, recourse is had to cellulose for general purpose moldings, other fillers including heat-resistant materials like fired asbestos, can be employed equally as well. Hence mineral-filled melamines can be produced which exhibit excellent thermal properties.

Curing conditions for typical melamine molding powders are illustrated in Figures 85 and 86.

Melamines possess better surface hardness and scratch resistance than the ureas, even though the latter are superior to most of the other common plastics in these respects. The melamines, however, are somewhat more brittle than the ureas and shatter more readily unless filled with impact-

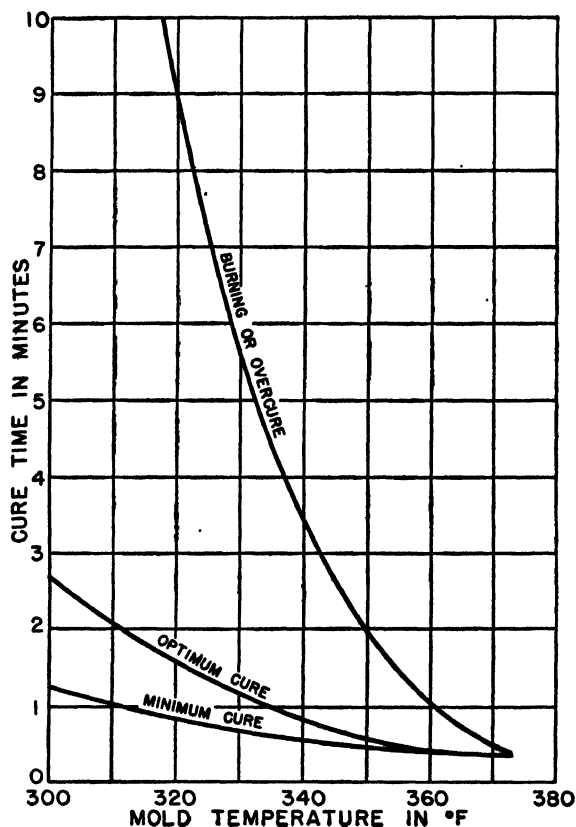


Figure 85. Mold temperature vs. curing time for "Melmac" alpha-cellulose filled materials (cross section: 0.070 inch). Optimum cure yields maximum resistance to moisture and cracking.

Courtesy American Cyanamid Co.

resisting fillers such as cotton or chopped fabric. The effect of heating upon impact strength of fabric-filled melamines is shown in Figure 87. Electrical insulating properties, including non-tracking characteristics, are good. Relationships between dielectric strength, temperature, and thickness, are shown in Figures 88 and 89. It is probable that the future will see considerable application of melamine molding powders. They are as yet too new and their supply has been too greatly hampered by war-time restrictions to permit general use. Because of the greater cost of

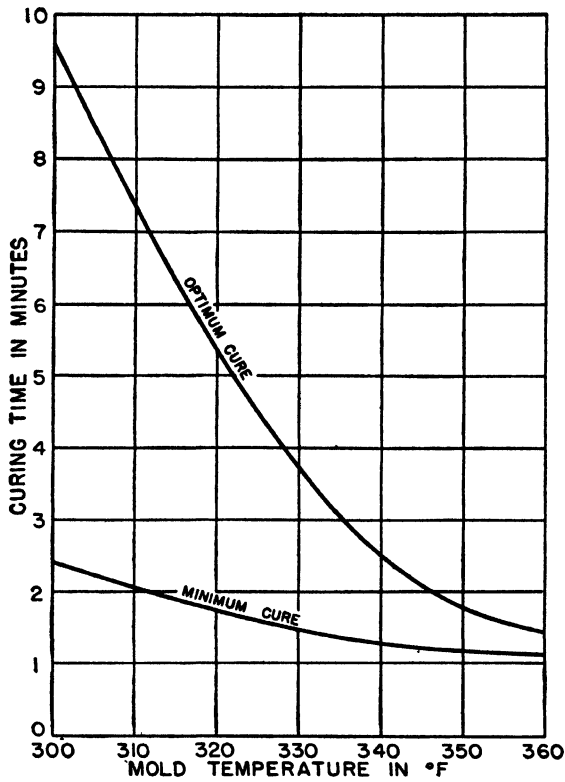


Figure 86. Mold temperature vs. curing time for "Melmac" chopped cotton fabric filled material (cross section: 0.125 inch)

Courtesy American Cyanamid Co.¹

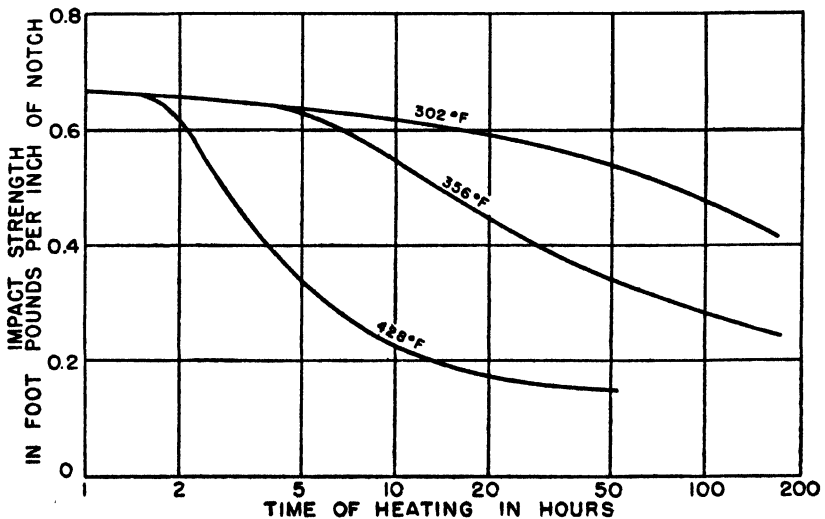
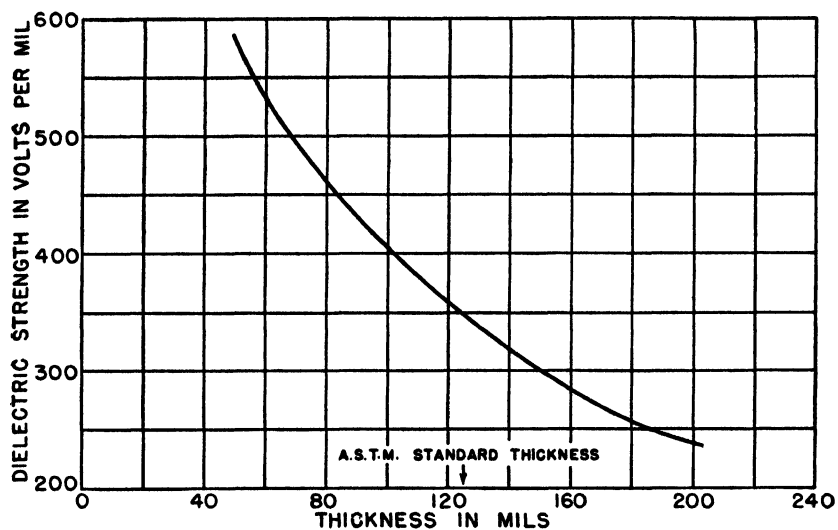
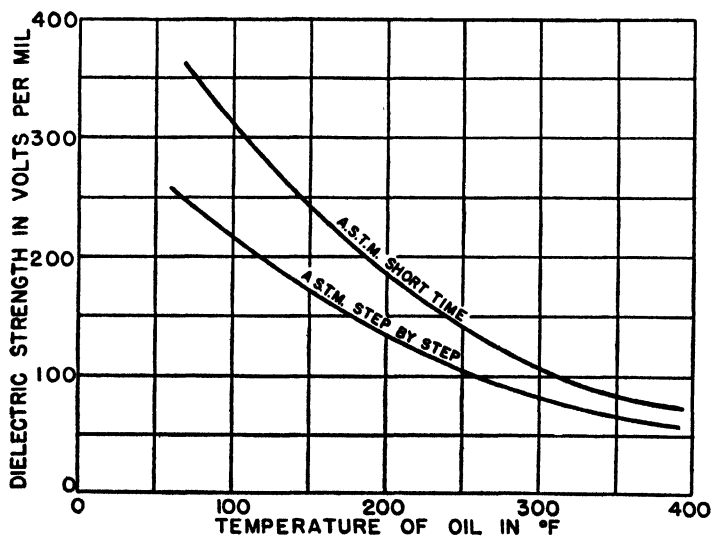


Figure 87. Effect of continuous heating on the impact strength of molded bars of fabric filled melamine. (Carswell and Nason⁷)



Courtesy American Cyanamid Co.¹

Figure 88. Dielectric strength of "Melmac" mineral filled material. ASTM short time test.



Courtesy American Cyanamid Co.¹

Figure 89. Dielectric strength of "Melmac" 592 mineral filled material ($\frac{1}{8}$ inch thick.)

melamine itself, these resins are considerably more expensive than the ureas.

Principal properties of molded melamine plastics are represented by those of "Melmec" listed below.

Principal applications of melamines to date have been in shatter-resistant tableware for the Navy, buttons, buckles, terminal blocks, and electrical parts.

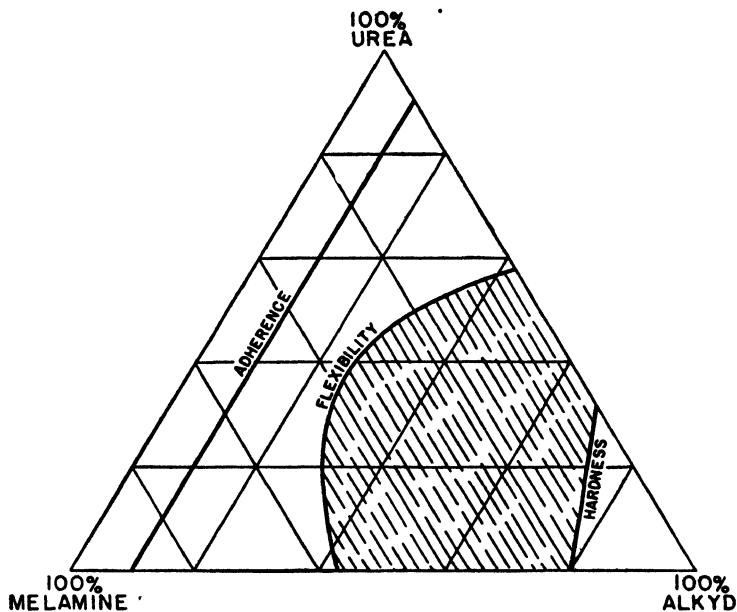


Figure 90. Typical triaxial diagram showing adherence, flexibility, and hardness of three-component systems of melamine, urea, and alkyd resins for surface coating applications. Formulations yielding enamels of satisfactory properties lie within the cross-hatched area. (Hodgins, Hovey, Hewett, Barrett, and Meeske¹⁰)

Molding powders are sold under the trade names "Catalin" melamine, "Melantine," "Melmec," "Plaskon" melamine, and "Resimene." In 1944, prices averaged 45 cents per pound.

Other Applications

The first American use of melamine resins was in the production of laminated materials, especially light-colored surface sheets bonded to phenolic bases. They are now used for this purpose by many of the principal laminators, especially for decorative applications where moisture condensation may be encountered. One of the earliest commercial applications of this kind was in surfacing the liner of electric refrigerator doors.

Physical Characteristics

Specific Gravity	1.49	1.4	1.7	1.98
Impact—Izod ft lb	.26	.686	.326	.325
Flexural—A.S.T.M., lb/sq in	14,000	14,000	9,280	11,180
Tensile Strength—A.S.T.M., lb/sq in	7,570	7,000	5,900	6,620
Coefficient of Expansion, in/in/°C				
— 45°	23×10^{-6}		22×10^{-6}	18×10^{-6}
+ 15°	44×10^{-6}		37×10^{-6}	22×10^{-6}
+ 75°	57×10^{-6}		30×10^{-6}	26×10^{-6}
Heat Distortion	410° F		266° F	410° F
H ₂ O Absorption—A.S.T.M.	0.68%	1%	0.13%	0.07%
Shrinkage—Mold in/in	.005"—.007"	.003"—.004"	.006"	.0057"
After 8 hr at 220° F	.004"—.005"	.002"—.003"	.001"	.0054"
After 48 hr at 220° F	.010"—.012"	.005"—.006"	.0027"	.0029"
Heat Resistance— $\frac{1}{8}$ " Test Piece	210° F	220°-250° F	300° F	375-400° F
—Up to $\frac{1}{2}$ "	210° F	220°-250° F	250° F	300° F+
—Up to 1"	210° F	220°-250° F	220° F	300° F+

Raw Material Characteristics

Particle Size	Powder and Granule	Chopped Cotton Cloth	Pass $\frac{1}{8}$ " Screen	Pass $\frac{1}{8}$ " Screen
Peakes Flow Range	Medium Hard	10-15 to 1	200-800 psi	100-450 psi
Bulk Factor	2.1		2.4	2.0
Apparent Density	.70 g/cc		.74 g/cc	.95 g/cc
Pourability	Excellent	Poor	Good	Good
Recommended Molding Pressure				
Compression, lb/sq in	2-4,000	2-6,000	1-6,000	1-5,000
Transfer, lb/sq in	—	10-30,000	6-20,000	4-20,000
Molding Temperature	300-340° F	275-330° F	280-360° F	265-365° F
<i>Chemical Resistance (Alpha-Cellulose Filled, "Melmac" 1077)</i>				
No change after 12 weeks immersion at 25° in the following:				
Tap Water	Dioxane	Ethylene Dichloride	Xylene	
10% Citric Acid	Methanol	Acetone	Liquid Soap	
10% C.P. Caustic	Butyl Cellosolve	Glycerol	0.5% Ivory Soap Solution	
	7.3% Aluminum Chloride Solution			

Concentrated Ammonia causes slight yellow discoloration.

40% Sulfuric Acid—1 week at 40°—bad discoloring and attack on surface.

Melamine resins are used in combination with other resins,—ureas, thioureas, phenolics, and particularly alkyds for light-stable surface coatings, especially where condensation of water may occur. For this purpose they are sold under the names "Melmac" and "Super Beckamine."

Figure 90 shows the relation between adherence, flexibility, and hardness of three-component blends of melamine, urea, and alkyd resins. This diagram was drawn up from experimental data upon twenty-one compositions. Those formulations satisfactory from the point of view of hardness, flexibility, and adherence lie within the cross-hatched area of this triaxial diagram.

Melamine resins are currently being developed for the hot-bonding of plywood, for paper impregnation, and for textile finishing. They are now used as impregnants to impart high wet strength to paper cartons employed by the Army. They have been utilized abroad for several years as textile finishing agents, especially in the manufacture of crease-resistant fabrics.

Other promising applications include leather treating, organolite manufacture, and fabric coating. Flexible melamine-alkyd resin coated fabrics are already being employed by the Army in suits of gas de-contamination squads.

Lower alkyl ethers of methylol melamines have been developed for the shrink-proofing of wool. Diammonium phosphate is employed as a catalyst to cause polymerization of the resin intermediate after application to the fabric. Products sold for this purpose are available under the trade-marks "Lanaset" and "Resloom"

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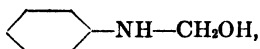
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Chapter 9

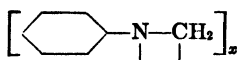
Aniline-Formaldehyde Resins

The products which can be obtained by causing organic amines to react with aldehydes cover a wide range of physical and chemical types. Careful control of reaction yields relatively simple, low molecular weight condensation compounds, but complex materials of moderately high molecular weight are more often the result. Resinous substances derived from the interaction of aniline, toluidine, and the naphthylamines with acetaldehyde, butyraldehyde, and acetaldol have been used for many years as vulcanization accelerators and antioxidants in rubber compounding. Moldable plastics produced from aniline and formaldehyde are of more recent origin and were first manufactured commercially in Switzerland by the Ciba Company. They were introduced into the United States about 1942.

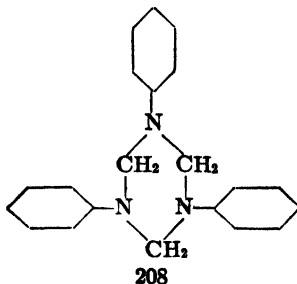
The initial product of reaction of formaldehyde with aniline appears to be an unstable addition compound,



which under the influence of heat or acid is rapidly dehydrated to polymers having the general formula



These products, for which various hypothetical formulas have been postulated without much proof, are both fusible and soluble. They are therefore probably linear polymers of relatively low molecular weight. They may also be formed by the action of heat upon anhydroformaldehyde aniline,



The properties of the polymers produced in the presence of acid may be varied by altering the ratio of aniline to formaldehyde. Excess aldehyde apparently reacts with the aromatic nucleus, introducing methylene bridges into the structure of the resin, for the greater the molar proportion of formaldehyde, the less soluble and less fusible are the products. Where the molar ratio of formaldehyde to aniline increases from 1.2 to 1.5, the temperature required for successful molding, for example, rises from 150–160° to over 200°.

Although commercially available aniline-formaldehyde resins are thermoplastic and can be removed only from cold molds, yet their degree of thermoplasticity is insufficient to admit of injection molding. This characteristic seriously hampers their general utility so that sheets and rods are the best known industrial forms of this plastic, despite the fact that molding powder is available under the name "Cibanite" and can be shaped at temperatures of 150–160° and pressures of 3000–6000 pounds per square inch.

Sheets and rods of aniline-formaldehyde plastic, but not tubes, are sold under the trade name "Dilectene" by the Continental Diamond Fibre Company. "Dilectene" is available in both 100 per cent resin form and in a plasticized grade, numbered 100 and 160 respectively.

In Great Britain aniline-formaldehyde resins are also fabricated in the form of paper base laminates under the trade name "Panilax." Resin is incorporated in the fiber during the paper-making process itself. The finished plastic contains from 45 to 50 per cent of amine-aldehyde condensation product.

These plastics are reddish-brown in color and translucent where unfilled. Moisture and oil absorption is small. Unplasticized grades show relatively good heat resistance and lack of cold flow as compared with most other thermoplastic resins; plasticized varieties are poor in both respects. These materials show good impact strength, weather well, are resistant to ultra-violet light, and are not attacked by most solvents. They are unaffected by alkalis, but are sensitive to acids. They can be machined easily. Plasticized grades can be punched and stamped. Physical properties of "Dilectene" are listed in Table 16.

Solubility characteristics of "Dilectene" are shown in Table 17.

Although interest in the plastics field has been directed primarily towards condensation products of aniline and formaldehyde, a new resin series based on diphenylamine has recently been introduced. Moldable condensation products can be obtained by reaction of one mole of the latter compound with amounts of formaldehyde ranging from 1.3 to 2 moles. As the quantity of aldehyde used approaches the upper limit, the plastic becomes substantially thermosetting.

Table 16. Properties of "Dilectene" ^a
($\frac{1}{8}$ in Sheet)

	"Dilectene" 100	"Dilectene" 160
Specific gravity	1.21	1.31
Hardness, Rockwell		
Room temperature	M-100-125	M-110-115
90°	M-105-115	Too soft
Hardness, scleroscope	85-95	83-90
Water absorption, 3 in by 1 in specimen (A.S.T.M. D570-40T)		
24 hours, per cent	0.08	0.03
144 hours, per cent	0.21	0.06
Tensile strength, psi	10,500	9,000
Flexural strength, psi	20,000	16,000
Modulus of elasticity in flexure, psi	740,000	1,800,000
Compression strength, flatwise, psi	20,000	20,000
Impact strength, Izod, $\frac{1}{2}$ in by $\frac{1}{2}$ in specimen, parallel to molding pressure, ft lb per inch of notch	0.33 ^b	0.38
Cold flow (A.S.T.M. D621-41T) $\frac{1}{2}$ in by $\frac{1}{2}$ in by $\frac{3}{8}$ in pileup, per cent reduction in height after 24 hours	0.17	16.35
Dielectric strength, volts per mil		
Short time,		
80° F	640	470
100° F	600	570
150° F	720	550
Step by step,		
80° F	410	430
100° F	520	490
150° F	650	480
Insulation resistance, megohms, after 4 days at 90 per cent RH, 95° F	96,000 (Unaffected by continued exposure)	62,000 (Decreased by continued exposure)
Distortion point (A.S.T.M. D48-39) (10 mil deflection under 5-lb load), ° F	210	125
Coefficient of linear thermal expansion (specimen 18 in long by 3 in wide by $\frac{3}{8}$ in thick), parts per million per ° F	30	Approx. 34

Table 17. Chemical Stability of "Dilectene" ⁵

Solvent or Reagent	"Dilectene" 100	"Dilectene" 160
Toluene	Not attacked	Plasticizer attacked
Benzene	" "	" "
Alcohol	" "	Not attacked
Acetone	" "	" "
Gasoline	" "	Plasticizer attacked
Epichlorhydrin	Attacked	Attacked
Dichlorhydrin	" "	" "
Amines (some)	" "	" "
Aniline	" "	" "
Weak acids	Slight attack	
Strong acids	Strong attack	
Hydrochloric acid, 1 %	Attacked	
Sulfuric acid, 1 %	" "	
Hydrochloric acid, conc.	" "	
Sulfuric acid, conc.	" "	
Acetic acid, 1 %	Not attacked	
Acetic acid, conc.	Attacked	
Formic acid	Strong attack	
Sodium hydroxide, up to 25 %	Not attacked	
Ammonium hydroxide (27-29 %)	No attack (absorption equal to that of H ₂ O)	
Effect of age	None	None
Effect of light	None	None
Burning	Will not support combustion	

Molded aniline-formaldehyde plastics are of merit especially because of their electrical properties. They are more resistant to tracking than the phenolics and retain good insulating characteristics not only at high frequencies, but also in the presence of moisture. Tables 18 and 19 summarize the electrical properties of "Dilectene."

Table 18. Variation of Loss Properties of "Dilectene" with Frequency ⁵

Frequency	Power Factor	Dielectric Constant	Loss Factor
<i>"Dilectene" 100</i>			
100 C	0.00226	3.72	0.0084
1 KC	0.00351	3.72	0.0130
10 KC	0.00595	3.68	0.0219
1 MC	0.00624	3.62	0.0226
10 MC	0.00469	3.60	0.0169
20 MC	0.00420	3.59	0.0151
50 MC	0.00425	3.58	0.0152
100 MC	0.00318	3.62	0.0115
<i>"Dilectene" 160</i>			
100 C	0.00495	3.56	0.0176
1 KC	0.00497	3.56	0.0177
10 KC	0.00703	3.48	0.0244
1 MC	0.00881	3.43	0.0302
10 MC	0.00778	3.41	0.0266
20 MC	0.00737	3.40	0.0251
50 MC	0.00702	3.37	0.0236
100 MC	0.00641	3.41	0.0218

Table 19. Variation of Loss Properties of "Dilectene" 100 upon Immersion in Water at Room Temperature (Measurements Made at 10^6 Cycles)⁵

Time Immersed	Power Factor	Dielectric Constant	Loss Factor
0	0.00650	3.66	0.0237
24 hours	0.00680	3.73	0.0250
48 hours	0.00700	3.77	0.0263
72 hours	0.00693	3.67	0.0253
96 hours	0.00664	3.73	0.0248
1 week	0.00683	3.70	0.0253
2 weeks	0.00713	3.81	0.0271
3 weeks	0.00845	3.83	0.0324

Principal applications of aniline-formaldehyde resins to date have been in the electrical field, especially radio and television.

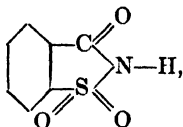
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Chapter 10

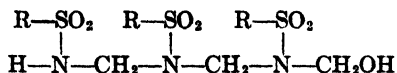
Aryl Sulfonamide-Formaldehyde Resins

Saccharin,



is made industrially by sulfonation of toluene with chlorosulfonic acid followed by conversion of the resultant *o*-toluene sulfonyl chloride into the sulfonamide by treatment with ammonia and oxidation of this compound to *o*-benzoyl sulfonamide which is then dehydrated. In the initial sulfonation reaction considerable quantities of *para* isomer are obtained despite the fact that chlorosulfonic acid is more favorable to formation of the *ortho* compound than is sulfuric acid. At 0°, for example, it is reported that chlorosulfonic acid yields 35 parts of *para*- to 65 parts of *ortho*-isomer. Attempts to utilize the by-product economically have resulted in the manufacture of such plasticizers as cyclohexyl *p*-toluene sulfonamide ("Santicizer" 1-H), mixed *o*- and *p*-toluene sulfonamides ("Santicizer" 9), mixed *o*- and *p*-toluene ethyl sulfonamides ("Santicizer" 8), and *o*-cresyl-*p*-toluene sulfonate, together with a series of resinous reaction products of *p*-toluene sulfonamide and formaldehyde.

The condensation of formaldehyde with aromatic sulfonamides appears to result first in the formation of an unstable methylol addition product which, upon loss of water, yields relatively low molecular weight condensation products. The molecular weight of the resin obtained from *o*-toluene sulfonamide and formaldehyde has been reported as averaging 400 in phenol solution. Hence, the following structural formula has been proposed for the major component of this type of resin:



where R is an aryl radical.

These materials are thermoplastic, melting to viscous liquids not far above room temperature. If a second sulfonamide group is introduced into

Table 20. Properties of Certain Toluene Sulfonamide Resins*

Color and form	"Santolite MS"	"Santolite MHP"	"Santolite K"
	Soft, pale yellow resin	Hard, brittle resin Nearly colorless lumps showing tendency to cold flow	Soft, viscous resin Slightly colored
Melting point (approximate)	50°	62°	Flows slowly at 30°
Flash point	146°	154°	204°
Specific gravity	1.355 at 25°	1.35 (approximate)	1.307 at 25°
Refractive index (approximate)	1.5690-1.5720 at 50°	1.5080-1.5110 (25% solution in toluene)	1.5370 \pm 0.003 at 50°
Acid number	Neutral	Neutral	10 Maximum
Solubilities	Soluble in alcohols, depositing permanently tacky films therefrom. Soluble in esters, ketones, and aromatic hydrocarbons from which hard films are obtained on drying. Soluble in glycerol. Soluble in acetic acid stronger than 72% by weight. Insoluble in aliphatic hydrocarbons and drying oils.		

* Manufacturers' Data. Monsanto Chemical Company.

the nucleus, thermosetting products are obtained upon reaction with sufficient formaldehyde.

To date, only thermoplastic sulfonamide resins are commercial articles. They are recommended especially for incorporation with cellulose acetate to increase the latter's retentivity of plasticizers and to reduce separation or exudation of plasticizer from acetate films. They can also be used to increase hardness and water-resistance of nitrocellulose films. They improve flexibility and toughness of ethyl cellulose—behavior not shown in combination with cellulose esters. The sulfonamide resins also find use with nitrocellulose or other resins in the production of heat-sealing lacquers.

Sulfonamide resins range in color from light yellow to water white. They are insoluble in water and aqueous acids, but dissolve in alkalis with slow decomposition. They are soluble in most organic solvents except aliphatic hydrocarbons and fatty oils, and are compatible with polyvinyl acetate and shellac as well as the cellulose derivatives previously mentioned. Upon heating, these resins give off a slight amount of formaldehyde, but an aldehyde odor is not present in films where they are combined with cellulose plastics.

Toluene sulfonamide resins are produced in the United States by the Monsanto Chemical Company under the trade name "Santolite." Properties of several of these materials are listed in Table 20.

In addition to the products listed in Table 20, several other "Santolites" are also manufactured. "K5," like "K," is an alkyd modification, and "BA," "BH," "BK," and "BK5" are derived from benzene instead of toluene.

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Chapter 11

Alkyds and Allied Resinous Esters

Many important synthetic resins and the majority of plasticizers are esters of more or less complicated nature derived from low molecular weight acids and alcohols. In this chapter attention will be fixed primarily upon alkyd resins which are made in great profusion by reaction of polybasic acids with polyhydric alcohols, with or without various modifiers. These resins are particularly useful in surface coatings. Their name, derived from *alcohol* and *acid*, and rewritten alkyd for euphony, was proposed in 1927 by R. H. Kienle of the General Electric Company's Research Laboratories, one of the pioneers in their commercial development.

HISTORY

Although of but recent industrial application, alkyds have been known for a century. It would seem inevitable that numerous products of this type should have been prepared and discarded in disgust, unrecorded, by early chemists seeking simple esters capable of ready purification by distillation or crystallization. The first published preparation of an alkyd was carried out in 1847 when, a year before his death, the great Swedish chemist, Jöns Jacob Berzelius, prepared glyceryl tartrate. Six years later, another alkyd, glyceryl camphorate, was made in France by Berthelot. In 1856, glyceryl esters of succinic acid and of citric acid were synthesized by Van Bemmelen and seven years later still similar products were studied by the Frenchman, Laurengo.

Not until 1901, however, is there any written account of attempts to esterify glycerol with phthalic anhydride. Even then, curiously enough, the purpose of the investigator, an Englishman by the name of Watson Smith, was to prepare an aliphatic analog of phenolphthalein! This chemist carried out a series of reactions between phthalic anhydride and glycerol, varying the conditions, but always obtaining a glass-like product. He suggested its use as a cement for chinaware and glass—an interesting remark inasmuch as one of its first technical applications some twenty years later was in bonding mica flake!

A few years afterwards, L. H. Friedburg, then Professor at the College of the City of New York, directed his attention to resinous products ob-

tained from the same reaction. Through the auspices of Herbert R. Moody, of the same school, Friedburg met A. McK. Gifford, of the General Electric Company, who obtained a sample of his material and subsequently succeeded in arousing the interest of the General Electric Company therein. This concern retained the services of Friedburg who called his product "Glyptal," a word adopted by G. E. as a trade name. It is commonly supposed to have been derived from glycerol and phthalic, but it is also said by one of Friedburg's coworkers to have been suggested by the expression glyptic (*i.e.*, structural) formula, inasmuch as it appeared possible to assign a glyptic formula to glyceryl phthalate, whereas the structural configuration of natural resins was then unknown.

Stimulated by Friedburg's work, the General Electric Company undertook a detailed investigation of resins of this general category between 1910 and 1916, obtaining a series of important patents granted to Callahan, Arsem, Friedburg, Howell, and Dawson. Later workers included J. G. E. Wright, Barringer, Kienle, Hovey, and others.

Phthalic anhydride, an essential intermediate for the manufacture of most of these resins, was then an expensive chemical, priced as high as \$4.25 per pound. The Gibbs and Conover method for producing this material by catalytic oxidation of naphthalene was developed in 1916. Commercial operation of the process soon resulted in a drop in price of the anhydride to but a small fraction of its former value, permitting its general use in the manufacture of important dyestuffs like alizarin and revivifying interest in alkyd resins.

"Glyptals" were first developed as bonding agents for mica flake. Applied in acetone solution, they yielded relatively inexpensive sheets having properties superior to those of shellac-pasted products. Flexible resin-bonded mica sheets were evolved later for various uses, including lamp shades and objets d'art. An oleic acid modified glyceryl phthalate was another of G. E.'s earliest commercial "Glyptals." It was used in 1921 as an insulating lacquer for brass lightning arrester electrodes. In the same year, Kienle conceived the idea of modifying alkyds with drying oils, but it was not until three years later, when others had also thought of the same thing, that he and Hovey began a series of investigations which, in 1933, resulted in the issuance of a broad American patent covering this field. Although earlier chemists had incorporated oleic acid and ricinoleic acid in alkyds, none—strangely enough—had employed the acids of drying oils. This development proved to be a great boon to the technology of these resins and was largely responsible for their phenomenal acceptance in surface coatings. Despite this fact, the Kienle patent, U. S. Patent No. 1,893,873, was declared invalid in 1935 when the General Electric Company sued the Paramet Chemical Company for

infringement. Several concerns had entered the alkyd field toward 1930. After invalidation of the Kienle patent, many others swelled the ranks of producers until today there are forty or more.

Another significant event of the 1920's was the discovery that both oil- and rosin-modified alkyds are compatible with nitrocellulose, yielding surface coatings showing both increased adhesion and gloss retention. This development led to enthusiastic acceptance of alkyd finishes by the automotive industry, first in combination with nitrocellulose, then alone.

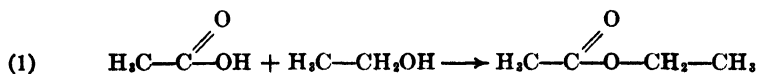
Many recent investigations have been directed toward production of flexible and rubber-like resins, some of which are made from dimerized drying oil acids.

Despite the fact that the bulk of domestic alkyd production is still destined for consumption in surface coatings, the greatest amount of published scientific information in this field deals with types that are not used directly as varnish vehicles. This situation has resulted from the fact that the development of alkyd surface coatings has grown largely along the lines of older varnish cooking methods, even though subjected to more scientific control. Commercial products have therefore often been the outgrowth of Edisonian methods of investigation.

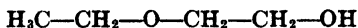
Alkyds have increased rapidly in volume during the last fifteen years. In 1944, American production amounted to over 245,000,000 pounds.

SIMPLE ESTERS: SOLVENTS, PLASTICIZERS, WAXES

Where a monohydric alcohol reacts with a monobasic acid, the product is a simple, low molecular weight ester that can usually be isolated easily in a pure state by distillation or crystallization. The formation of ethyl acetate is typical:



Many acetates, propionates, butyrates, and other esters of lower aliphatic alcohols and glycol monoethers like "Cellosolve,"



are invaluable solvents, widely used in the formulation of cellulose nitrate lacquers, to mention but a single example.

As the molecular complexity of either acid or alcohol, or both, increases, the nature of the ester becomes correspondingly complicated.

Several high-boiling, relatively non-volatile liquid esters of monofunctional acids and alcohols find use as plasticizers in coatings, plastics, and allied products. Butyl stearate, butoxyethyl stearate ("KP-23"), methoxyethyl oleate ("Kapsol"), methyl abietate ("Abalyn"), and hydro-

generated methyl abietate (Hercolyn") are but a few of the important plasticizers of this group.

Several solid aliphatic esters of this category such as cetyl palmitate (spermaceti) and melissic palmitate (beeswax) are natural waxes.

ESTERS OF MODERATELY COMPLICATED STRUCTURE: PLASTICIZERS, OILS, ESTER GUM

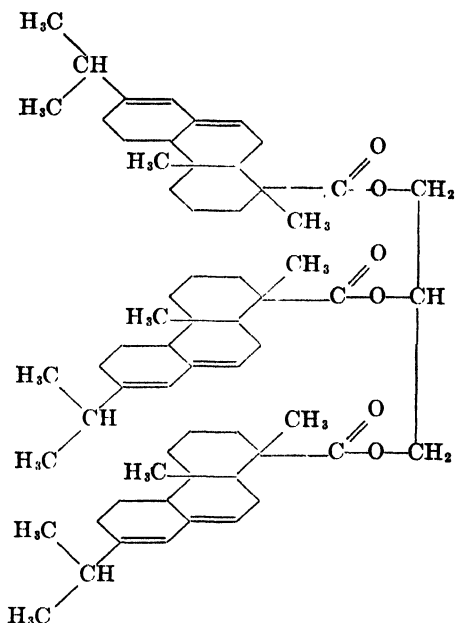
If either (but not both) the alcohol or acid reacting to form an ester is bi- or poly-functional, the product is still relatively simple. A considerable number of plasticizers belong to this category. Typical commercial products of this kind are listed below:

- diethyl phthalate
- dibutyl phthalate
- di-2-ethylhexyl phthalate ("Flexol" DOP)
- dicapryl phthalate
- dimethoxyethyl phthalate ("Methox")
- diethoxyethyl phthalate ("Ethox")
- dibutoxyethyl phthalate ("Kronisol")
- triphenyl phosphate
- tricesyl phosphate ("Kronitex" AA, "Lindol")
- diphenyl mono-*o*-xenyl phosphate ("Dow Plasticizer 5")
- dibutyl sebacate
- dibutyl tartrate
- sorbitol dilaurate
- diethylene glycol dipropionate ("KP-45")
- triethylene glycol di-2-ethyl-butyrate ("Flexol" 3 GH)
- triethylene glycol di-2-ethyl-hexoate ("Flexol" 3 GO)
- triethylene glycol esters of coconut oil fatty acids ("SC" plasticizer)
- methyl phthalyl ethyl glycolate ("Santicizer" M-17)
- ethyl phthalyl ethyl glycolate ("Santicizer" E-15)
- butyl phthalyl butyl glycolate ("Santicizer" B-16)
- dimethylcyclohexyl adipate ("Sipalin" AOM)
- ethylene glycol diabietate ("Flexalyn" C)
- diethylene glycol diabietate ("Flexalyn")
- hydrogenated diethylene glycol diabietate ("Staybelite" Ester No. 2)

Fatty oils, being glycerol derivatives, also belong in this class of esters. In the case of drying oils, their molecular complexity coupled with attendant potentialities for polymerization or intermolecular linkage by oxidation or sulfurization, have led to innumerable technical applications of vital importance in paints, varnishes, printing inks, linoleum, oil cloth, rubber extenders (factice), and divers other products.

Where the molecular weight of the reactants is relatively great and their structure sufficiently complicated, resinous characteristics begin to appear. Thus ester gum, made by numerous manufacturers, is used as a component of spar varnishes. It is derived from rosin by esterification with glycerol. It consists primarily of glyceryl triabietate which, accord-

ing to present conceptions of the structure of abietic acid, should possess the formula shown below, with a molecular weight of 944:



Hydrogenated rosin, sold under the trade name "Staybelite," is esterified with glycerol. The product is used as a tackifying resin in adhesives. Glycol and polyglycol esters of hydrogenated rosin and of polymerized rosin are available as variously numbered "Staybelite" and "Poly-Pale" esters, respectively, and are recommended for use in adhesives, printing inks, and allied products.

Rosin esters of pentaerythritol, $C(CH_2OH)_4$, are sold under the name "Pentalyn" for varnish applications. They are harder than ester gum, softening at higher temperatures.

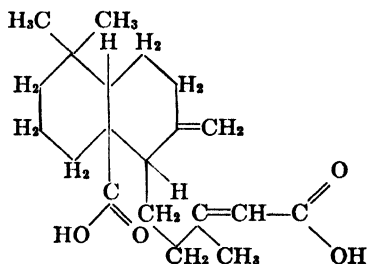
"Vinsol," a dark-colored, acidic resin derived from products of the naval stores industry, can also be esterified with glycerol.

Physical properties of a number of Hercules' rosin derivatives are listed in Table 21.

Other varnish vehicles more or less analogous to ester gum are manufactured from a few natural resins. Most important are glyceryl esters of several cracked copals, especially Congo gum.

Run Manila and Pontianak are occasionally esterified. In other cases, such as Kauri and dammar, no substantial improvement in properties is obtained by esterification because of the low acidity of the run resins, as indicated in Table 22.

In order to convert many natural resins to forms which will dissolve in drying oils, the varnish industry has long followed the practice of "running" them. This process is substantially a cracking operation in which Congo, for example, is heated to 330–345° until it is sufficiently broken down to dissolve in oils—a point usually determined by visual inspection of the viscosity of the oil draining from the stirring paddle. In running copals before esterification with glycerol, the cracking must proceed farther than in processing for direct varnish formulation; otherwise gelation will occur upon reaction with glycerol. Dibasic acids like agathic acid,



and other polybasic polyterpene acids are characteristic of these fossil or semi-fossil resins. It will be seen from p. 236 of this chapter that such polybasic acids should react with glycerol to yield cross-linked gels. It would therefore appear that run copals have been pyrolytically decarboxylated.

Mixed glyceryl esters of rosin and Congo are also manufactured as varnish vehicles.

RESINOUS ESTERS OF POLYFUNCTIONAL ALCOHOLS AND ACIDS: ALKYDS

If both alcohol and acid employed in esterification are bi- or polyfunctional, the products are usually much more complex than those described thus far. Most reactions of this category lead to the formation of high polymers and it is to such products that the general term alkyd has been applied.

By varying the nature of the reactants, a wide range of products can be obtained. The many different types of alkyds can be classified as follows:

(A) Polyesters of bifunctional reactants

I. Saturated

II. Unsaturated

(a) Low in maleic unsaturation

(b) Medium to high in maleic unsaturation

Table 21. Physical Properties of Synthetic Resins Produced from Rosin¹⁵

Trade Name	Type of Rosin Derivative	Acid Number	Rosin	Color	Lowbond	Melting Point (°C)
Abalyn	Methyl ester	8 ¹	—	—	20A or less	Viscous liquid
Hercolyn	Hydrogenated methyl ester	8 ¹	—	—	8A or less	Viscous liquid
Flexalyn	Diethylene glycol ester	5-10	—	—	20-40A	45-50
Flexalyn C	Ethylene glycol ester	4-8	—	—	20-40A	63-68
Staybelite Ester No. 10	Glycerol ester of hydrogenated rosin	10 ¹	N ¹	—	—	83-86
Staybelite Ester No. 1	Ethylene glycol ester of hydrogenated rosin	12 ¹	N ¹	—	—	55-58
Staybelite Ester No. 2	Diethylene glycol ester of hydrogenated rosin	10 ¹	N ¹	—	—	38-45
Pentalyn A	Pentaerythritol ester	19 ¹	—	—	25-38A	110 ²
Pentalyn G	Pentaerythritol ester	19 ¹	—	—	25-39A	131 ²
Pentalyn X	Pentaerythritol ester	15	—	—	35A	155 ²
Pentalyn M	Phenolic modified pentaerythritol ester	25 ¹	H-M	—	—	165 ²
Poly-pale Ester Gum	Glycerol ester of polymerized rosin	8-10	WW-WG	—	—	116-118
Poly-pale Ester No. 1	Ethylene glycol ester of polymerized rosin	8-10	—	—	40-45A	80-85
Poly-pale Ester No. 2	Diethylene glycol ester of polymerized rosin	10-12	—	—	60A	61
8L Ester Gum	Glycerol ester of pale wood rosin	6-8	WG-N	—	—	92-96
Vinsol Ester Gum	Glycerol ester of Vinsol rosin	6	—	Black	—	144-148

¹ Maximum ² Minimum

Table 22. Physical and Chemical Properties of Run Resins ⁴³

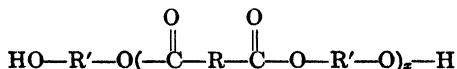
Name of Resin	Per Cent Loss	Softening Point (°C)	Melting Point (°C)	Melting Point (°F)	Specific Gravity	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number
Batavia dammar, A/D									
Batavia dammar, A/E	10	80	176	248	1.04	13	17	22	107
Batu east india nubs and chips	10	70	158	230	1.04	10-15	17	15	119
Black east india bold scraped	10-15	95-115	203-239	275-320	1.04	15	33	36	95
Boea hard bold amber	10-15	110-120	230-248	275-293	1.03	12-15	14	36	88
Congo No. 1 water-white transparent	20-25	105	221	257-275	1.06	78-85	86	91	106
Congo No. 4 pale bold straw	25	70-80	158-176	230-248	1.04	40-60	53	64	88
Congo No. 11 hard dark amber bold	25	80-90	176-194	221-230	1.05	60-80	75	82	89
Congo No. 21 selected nubs ordinary	25	80-90	176-194	239-257	1.04	60-75	68	72	85
Kauri No. 2 brown	20-25	80-90	176-194	239-257	1.05	60-75	76	81	85
Kauri No. 2 pale	20-25	80	176	248-266	1.06	12-20	16	27	79
Manila CBB	25	80-90	176-194	239-248	1.06	20-30	21	36	87
Manila DBB	25	85-90	185-194	257-275	1.05	60	67	70	99
Manila loba C	20	85-90	185-194	257-266	1.05	50-60	53	67	96
Pale east india macassar nubs	10-15	100	212	284-293	1.04	55-65	72	89	104
Pale east india Singapore nubs	10-15	110	230	275-284	1.04	12-15	22	21	95
Philippine manila bold pale chips	20	85	185	261	1.06	9-14	16	17	89
Pontianak bold scraped	20-25	105	221	257-266	1.06	50-55	62	72	93
					1.06	75-85	92	86	99

- (c) Possessing non-maleic unsaturation
 - (1) From dimerized fatty acids
 - (2) From drying oil acids
- (B) Polyesters of polyfunctional reactants.
 - I. Unmodified (straight alkyds)
 - II. Non-drying oil modified
 - III. Drying oil modified
 - IV. Rosin and natural resin modified
 - V. Synthetic resin modified
 - (a) Phenolic modified
 - (b) Urea or melamine modified

Polyesters of Bifunctional Reactants

Saturated Polyesters

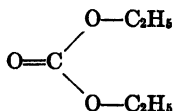
As a rule, where a dibasic acid, $R(CO_2H)_2$, reacts with a dihydric alcohol, $R'(OH)_2$, the product is a linear polyester which may be terminated by either carboxyl or hydroxyl groups, or both, depending largely upon the molecular ratio of the reactants. If both end-groups are hydroxyls, the general formula is:



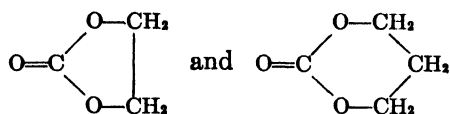
Polyfunctional acids and alcohols, on the other hand, react with each other to form cross-linked, tridimensional esters as the final products, provided at least one of the intermediates contains more than two reactive groups. There is, therefore, a marked difference between polyesters prepared from bifunctional reactants only and alkyds made from polyfunctional intermediates. The former possess linear structures which are non-convertible by heat and are permanently thermoplastic unless the presence of double bonds or other reactive groups permits cross-linking by addition polymerization, oxidation, or vulcanization. These exceptions will be discussed later.

Cyclic Esters. In certain special cases, cyclic esters may be obtained by esterification of bifunctional acids and alcohols. Where the nature of reactants is such that low molecular weight, monocyclic, 5- or 6-membered rings can be produced, their formation is favored. Where 7 or more members would be present in the resultant monocyclic ester, linear molecules predominate and are usually the sole result.

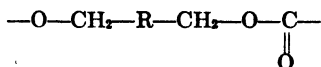
Carbonic acid is the simplest bifunctional organic acid. Although it cannot be esterified directly, glycol carbonates can be obtained by ester interchange between diethyl carbonate,



and various glycols in the presence of metallic sodium. Ethylene glycol and trimethylene glycol yield monocyclic esters containing 5 and 6 ring members respectively, *i.e.*:

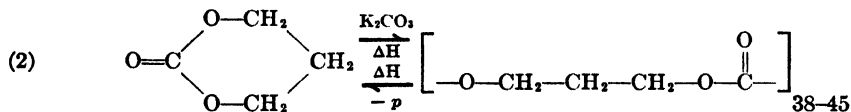


Higher glycols, on the other hand, yield linear polycarbonates possessing the structural unit



where the degree of polymerization may vary from 5 to 20. The formation of large rings is not observed.

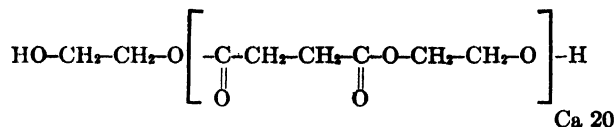
It is of interest to note that six-membered cyclic esters are capable of exhibiting reversible transformation to linear polymers. Trimethylene carbonate, for example, upon heating is converted to a linear polyester. This reaction is catalyzed by small amounts of potassium carbonate; traces of moisture, also, are probably necessary. The polymer, in turn, can be easily depolymerized to the cyclic monomer by distillation in vacuo.



Other linear polyesters can be depolymerized, less readily and less completely, to monomeric or dimeric macrocyclic esters by heating just below their points of thermal decomposition at pressures below 1 mm, usually in the presence of a catalyst favoring ester interchange. Metallic sodium is effective in facilitating this reaction where polycarbonates, oxalates, or malonates are involved. More satisfactory catalysts in the case of polyesters of other dibasic acids include hydrated chlorides of bivalent tin, manganese, iron and cobalt, metallic magnesium and its oxide, carbonate and chloride, and manganous carbonate. Macrocyclic esters can thus be formed, containing even as many as 16 or more members in the ring. They tend to be reconverted to linear polymers upon prolonged heating at 200°, especially in the presence of catalytic amounts of potassium carbonate.

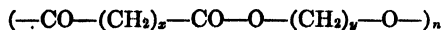
Saturated Linear Polyesters. By direct esterification, Carothers and his coworkers prepared a considerable number of linear polyesters ranging from trimethylene oxalate to decamethylene sebacate, as well as several phthalates. The average molecular weight of polyesters of this type, prepared by simply heating the reactants together with stirring, is in the order of 3000. Oxalates and carbonates range upwards from 1100. Phthalates run from 1800 to 5000, corresponding to degrees of polymerization of 7 to 25. The lower glycols give the highest degree of condensation polymerization.

Whether the end groups of a linear polyester are hydroxyl or carboxyl radicals depends to some extent upon the molecular ratio of the reactants. Succinic acid esterified with excess ethylene glycol yields a fairly homogeneous neutral polyethylene succinate of molecular weight about 3000, in which both terminal groups are hydroxyls:



Upon esterification with excess acid, a polymeric mixture is produced in which acidic esters predominate. The average molecular weight of the mixture can be controlled to some extent, although not with much precision, by adjusting the amount of excess acid.

Most linear polyesters derived from ethylene glycol are solids. A few, notably ethylene malonate, are liquids at room temperature. Diethylene and polyethylene glycols frequently yield liquid or balsamic products. In contrast to polyesters from phthalic anhydride, solid, saturated aliphatic polyesters of the general formula



present the interesting phenomenon among high polymers of possessing crystallinity, although the crystals are always microscopic or submicroscopic in size and are often not clearly defined. X-ray examination almost always gives evidence of crystallinity in esters of this type. Crystallized ethylene succinate and decamethylene sebacate as precipitated from solution are dusty powders which are prone to acquire a static electric charge. As usually prepared, however, they are brittle waxes. Intermediate members of the series are more soft and tend to be somewhat sticky. In general, adipates melt at lower temperatures than the corresponding succinates and sebacates while, with a given acid, trimethylene glycol esters usually show lower melting points than other unbranched glycol esters.

Softening points of a series of linear polyesters prepared by Carothers

Table 23. Polyesters from Glycols and Dibasic Acids¹⁶

Compound	Formula of Structural Unit	Atoms in Chain of Structural Unit	Average Observed Molecular Weight	Average Number of Structural Units per Molecule	Physical Properties
Tetramethylene carbonate	$\text{O}-(\text{CH}_2)_4-\text{O}-\text{CO}-$	7	1400	11-12	Microcrystalline powder, m.p. 59°
Pentamethylene carbonate	$\text{O}-(\text{CH}_2)_5-\text{O}-\text{CO}-$	8	2700	20-22	Microcrystalline powder, m.p. 44-46°
Hexamethylene carbonate	$\text{O}-(\text{CH}_2)_6-\text{O}-\text{CO}-$	9	2800	18-21	Microcrystalline powder, m.p. 55-60°
Decamethylene carbonate	$\text{O}-(\text{CH}_2)_{10}-\text{O}-\text{CO}-$	13	1800	8-10	Microcrystalline powder, m.p. 55°
Ethylene succinate	$\text{O}-(\text{CH}_2)_2-\text{O}-\text{CO}-(\text{CH}_2)_2-\text{CO}-$	8	3000	20	Microcrystalline powder, m.p. 108°
Ethylene adipate	$\text{O}-(\text{CH}_2)_2-\text{O}-\text{CO}-(\text{CH}_2)_4-\text{CO}-$	10	2900	17	Microcrystalline powder, m.p. 50°
Hexamethylene succinate	$\text{O}-(\text{CH}_2)_6-\text{O}-\text{CO}-(\text{CH}_2)_2-\text{CO}-$	12	3400	14	Microcrystalline powder, m.p. 57°
Ethylene sebacate	$\text{O}-(\text{CH}_2)_2-\text{O}-\text{CO}-(\text{CH}_2)_8-\text{CO}-$	14	4000	13	Microcrystalline powder, m.p. 79°
Trimethylene sebacate	$\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_8-\text{CO}-$	15	3100	12	Microcrystalline powder, m.p. 56°
Decamethylene adipate	$\text{O}-(\text{CH}_2)_{10}-\text{O}-\text{CO}-(\text{CH}_2)_4-\text{CO}-$	18	3000	10	Microcrystalline powder, m.p. 77°
Decamethylene sebacate	$\text{O}-(\text{CH}_2)_{10}-\text{O}-\text{CO}-(\text{CH}_2)_8-\text{CO}-$	22	3000	8	Microcrystalline powder, m.p. 74°
Ethylene phthalate	$\text{O}-(\text{CH}_2)_2-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-$	8	4800	25	Hard, transparent resin
Trimethylene phthalate	$\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-$	9	3100	14	Soft, transparent resin
Hexamethylene phthalate	$\text{O}-(\text{CH}_2)_6-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-$	12	1800	7	Soft, transparent gum
Decamethylene phthalate	$\text{O}-(\text{CH}_2)_{10}-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-$	16	2100	7	Very viscous, transparent sirup
Trimethylene oxalate	$\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-\text{CO}-$	7	2000	15	Microcrystalline powder, m.p. 88°
Hexamethylene oxalate	$\text{O}-(\text{CH}_2)_6-\text{O}-\text{CO}-\text{CO}-$	10	1100	7	Microcrystalline powder, m.p. 66°
Decamethylene oxalate	$\text{O}-(\text{CH}_2)_{10}-\text{O}-\text{CO}-\text{CO}-$	14	1200	6	Microcrystalline powder, m.p. 79°
Polyester from hydroxydecanoic acid	$\text{O}-(\text{CH}_2)_9-\text{CO}-$	11	5000	20	Microcrystalline powder, m.p. 76° (30)

and his associates are listed in Table 23, together with average molecular weights determined by cryoscopic or ebullioscopic means.

By heating linear polyesters at temperatures in the neighborhood of 200° for several days in a molecular still, Carothers and Hill found it possible to continue condensation to form what they called superpolyesters, distinguishing the latter by the Greek prefix ω , as contrasted with the designation α , applied to lower polymers obtained under normal conditions. Similar, although less marked conversion of α to ω -esters can be brought about by long-continued heating of the former at ordinary pressures in thin layers in a current of nitrogen, or by bubbling nitrogen through molten α -ester.

Carothers and Hill set the line of division between α and ω polyesters at a molecular weight of 5000, although most of the latter are above 10,000. Table 24 compares the properties of α - and ω -esters obtained from trimethylene glycol and hexadecamethylene dicarboxylic acid.

Superpolyesters are harder and tougher than the corresponding α -esters. Solvents first swell them, then yield solutions of high viscosity. Like the α -polyesters discussed above, ω -esters are crystalline in character, as shown by x-ray powder diagrams. They lose their crystallinity a little below their softening point and, while molten, can be drawn into filaments. If these filaments are spun under tension, or if a cold filament is stretched at room temperature or slightly above, it loses its opacity, increases permanently in length at the expense of its diameter, and becomes strong and pliable. X-ray examination shows the cold-stretched filament to be in a highly oriented state.

Table 24. Properties of α - and ω -Polyesters from Trimethylene Glycol and Hexadecamethylene Dicarboxylic Acid ¹⁸

	α -Ester	ω -Ester
Apparent mol. wt.	3,000	12,000
At 100° C	Viscous liquid	Soft, sticky resin
At room temperature	White, opaque, brittle wax; d_{20}^{20} 1.061	Cream colored, opaque, horny, elastic; d_{20}^{20} 1.058
Melting point, ° C	75-76	Becomes transparent at 75, but does not flow
Solubility	Very soluble in cold CHCl_3 . Readily soluble in hot ethyl acetate; separates on cooling as a microcrystalline powder	Swells in cold CHCl_3 , then dissolves. Swells and slowly dissolves in hot ethyl acetate; separates on cooling as a white, amorphous, curdy precipitate
Relative viscosity of 7.3% weight solution in chloroform (chloroform, 216 seconds = 1 unit)	8.6 units	166 units

As the molecular structure of linear polyesters decreases in symmetry, these compounds lose their tendency to crystallize. This effect is especially noticeable in the case of phthalates. They are either non-crystalline, hard, tough, and glass-like resins at room temperature or viscous liquids. In general, softness of linear phthalates increases with increasing chain length of the glycol.

In kinetic studies of the esterification of phthalic anhydride with ethyl-

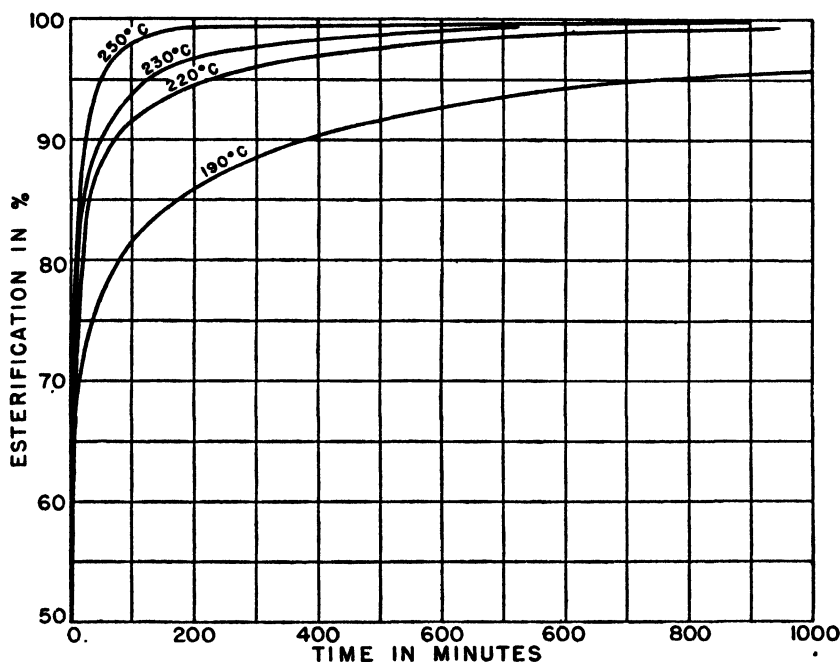


Figure 91. Isotherms showing the course of esterification of stoichiometric amounts of ethylene glycol and phthalic anhydride. (Kienle and Hovey³⁶)

ene glycol, Kienle and Hovey showed the reaction to be strongly exothermic at the beginning, during which time it proceeds very rapidly. It should be noted, however, that the exotherm in this case is caused by reaction of the anhydride and is not general for polyesterifications. Under isothermal conditions and at temperatures of 190°, or above, reaction between phthalic anhydride and ethylene glycol is almost half over within the first minute. The relation between the degree of esterification and time of reaction at a given temperature is shown in Figure 91.

Because of the linear nature of the resin produced no gelation occurs, regardless of the length of heating; hence esterification can be carried

nearly to completion. Figure 92 shows the dependence of flow point of the polyester upon time of reaction at 190°.

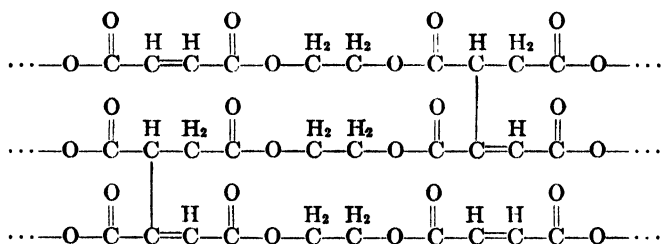
As shown in Figure 93, the time required to attain 95 per cent esterification is a logarithmic function of the reciprocal of the absolute temperature.

Relatively few non-convertible linear alkyds are produced commercially. A small number of balsams of this type, based on phthalic, succinic, and sebacic acids are available as plasticizers for nitrocellulose, various elastomers, and other resins. They are also employed to some extent in caulking compounds and adhesives. Typical of such products are some of the "Rezyls" and "Paraplexes."

Unsaturated Linear Polyesters

Saturated linear alkyds produced by esterification of dihydric alcohols with dibasic acids are non-convertible by heat. That is to say, they are permanently thermoplastic. If, however, unsaturated reactants are utilized instead of fully saturated ones, the resulting polyesters may be heat convertible as the result of reactions other than esterification. This phenomenon has been noted especially in the case of ethylene and polyethylene glycol esters of maleic and fumaric acids. The transformation of soluble, fusible polymaleates to insoluble, infusible products appears to be the result of the establishment, by addition polymerization, of direct carbon-to-carbon linkages between the chains at points of unsaturation. This behavior is comparable to the heat-bodying of drying oils. Thermal conversion of unsaturated linear polyesters is accelerated by light, heat, and such catalysts as cobalt salts and benzoyl peroxide. It is deterred by typical polymerization inhibitors like hydroquinone.

The structure of a portion of a cross-linked glycol maleate may be typified by the following illustrative formula:



Linear heat-convertible polyesters produced by the reaction of dihydric alcohols with such unsaturated dibasic compounds as maleic anhydride can also be converted by oxidation to insoluble, infusible products. Oxidation can be brought about either with or without the aid of driers. In this

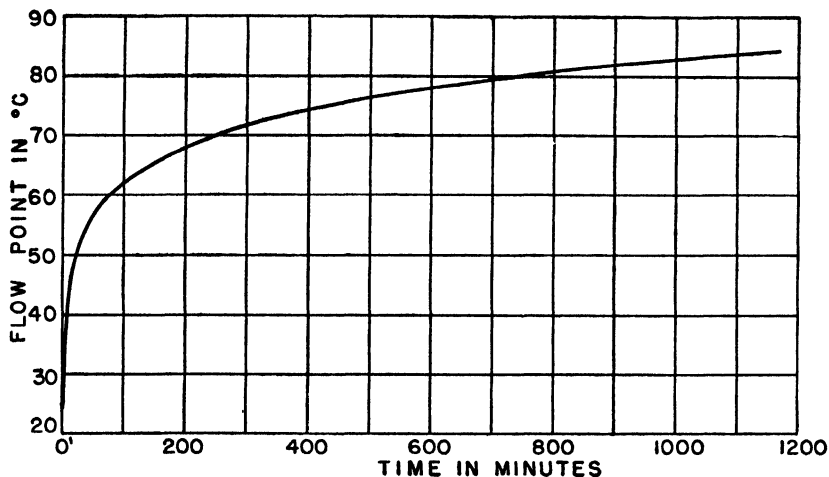


Figure 92. Flow point of the reaction product of stoichiometric amounts of ethylene glycol and phthalic anhydride *vs.* time of esterification at 190°. (The flow point here reported is that temperature at which a small sample of resin [0.50 inch thick] will flow under gravity a vertical distance of 0.20 inch when subjected to a gradual increase in temperature of 2–3° per minute.) (Kienle and Hovey^{35, 36})

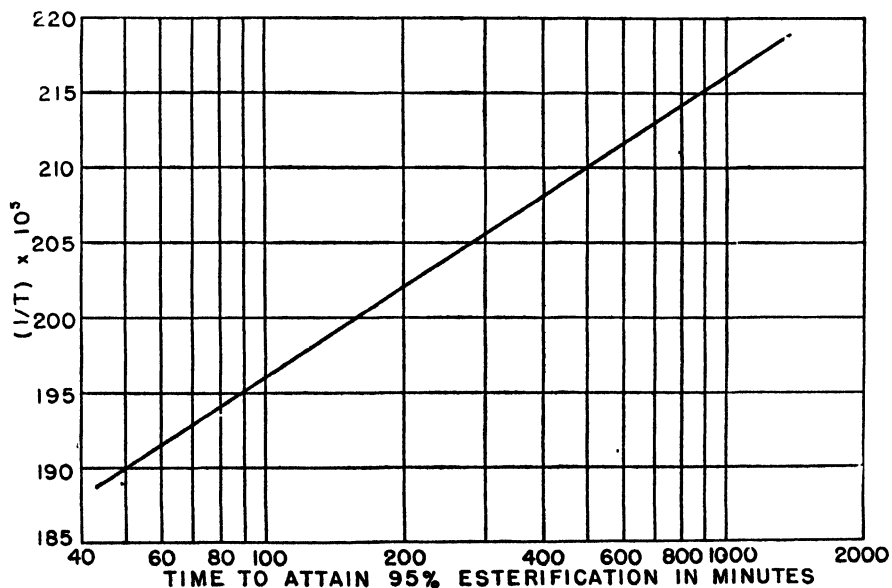


Figure 93. Time required to attain 95 per cent esterification of stoichiometric amounts of ethylene glycol and phthalic anhydride *vs.* reciprocal of the absolute temperature. (Kienle and Hovey³⁶)

respect, as in heat conversion, these resins resemble drying oils. They can, moreover, be modified with the acids of drying oils, to yield resins which are still more easily converted to insoluble, infusible forms by oxygen.

Linear Polyesters of Low Maleic Unsaturation. Linear alkyds possessing only a relatively small amount of unsaturation can still be cross-linked by means of heat and peroxide catalysts. It is therefore possible to produce curable polyesters by reaction of a glycol, a saturated aliphatic dibasic acid, and a minor quantity of maleic acid. From 3 to 4 mole per cent of the latter usually imparts satisfactory curing properties.

Where the degree of polymerization of the alkyd is sufficiently high and where the number of methylene groups separating the carboxyls of the initial reactants is great enough (as in glycol or mixed ethylene and propylene glycol esters of sebacic acid, for example, modified with maleic acid) the products obtained upon curing with benzoyl or lauroyl peroxide are rubber-like in character, even though the linear alkyds, before cross-linking, are hard, waxy, and more or less crystalline. Prior to curing, alkyds of this kind may be compounded on rubber rolls with such fillers as iron oxide or calcium carbonate. Carbon black is not suitable inasmuch as it impedes the catalytic action of benzoyl peroxide. Certain soft carbon blacks may, however, be used in conjunction with *ter*-butyl hydrogen peroxide. Cured stocks possess tensile strengths ranging from 1200 to 1800 pounds per square inch and elongations varying from 200 to 450 per cent.

Several compositions of this type are shown in Table 25, together with their rubber-like qualities.

The products often exhibit a tendency to stiffen on aging because of partial recrystallization. Reheating or flexing restores initial flexibility. They are moderately oil resistant, typical compounded materials swelling about 5 per cent in ethyl alcohol and 55 per cent in benzene after seven days' immersion at 76° F. Toluene-swollen products, however, break readily upon sharp flexing and tend to crumble upon rubbing. After evaporation of solvent, they retrieve their original properties. Products of this kind, developed by the Bell Telephone Laboratories, have been named "Paracon." The uncured polyesters are available from the Resinous Products and Chemical Company under the trade name "Paraplex" X-100.

Improved products are under development.

Work at the Bell Laboratories indicates that in certain instances, at least, entirely saturated linear polyesters can be cross-linked by heating with 4 to 5 per cent of benzoyl peroxide. In such cases inter-skeletal bridges are thought to be established between the carbon atoms adjacent to the esterified carboxyl groups. A small amount of unsaturation, nevertheless, facilitates cross-linking.

Table 25. * Composition and Properties of Two Natural Rubber Stocks (JK-100 and JK-101)
Compared with Several Typical Paraplex X-100 Vulcanizates ^a

Compound	JK-100 ^b	JK-101 ^b	JK-159	JK-160	JK-161	JK-162	JK-170	JK-171	JK-183 ^c	JK-184 ^d	JK-193	JK-218	JK-318	JK-575
Pale Crepe	200	200												
Paraplex X-100			200	200	200	200	200	200	200	200	200	200	200	200
Lupercio A			4.35	8.7	4.35	8.7	4.35	8.7	8.7	8.7	17.4	8.7	8.7	8.7
Kalvan		165			158	158						123		
Mapico Red	297								400	150				
Suprex Clay		313	300	300			152	152			152			
Rayox												50		
C-741													137	
Silene														170

15 Minutes
at 45 lbs

All Paraplex X-100 vulcanizates cured for 10 minutes at 20 lbs steam pressure

Cure
Properties

Tensile (psi)

% Elongation

% Permanent Set ^e

2400	2968	1512	1640	1608	1428	1180	1228	1460	1568	1320	1792	1783	1200
582	713	440	407	410	380	407	397	360	417	357	363	407	233
35	56	16	14	11	6	45	40	16	6	40	9	15	11

^a All stocks loaded to 31 volume per cent unless otherwise noted.

^b Stocks JK-100 and 101 are natural rubber stocks and contain, in addition to pale crepe and pigment shown, 10.6 parts zinc oxide, 5.5 parts sulfur, 2 parts stearic acid, 2 parts phenyl beta naphthylamine, 2 parts benzothiazyl disulfide, and 0.2 parts tetramethyl thiuram disulfide.

^c Duplication of Stock JK-160 except an increase of 33 1/3% in volume loading.

^d Duplication of Stock JK-160 except a decrease of 50% in volume loading.

^e Permanent Set determined by measuring the distance between one inch marks of broken test specimen ten minutes after break.

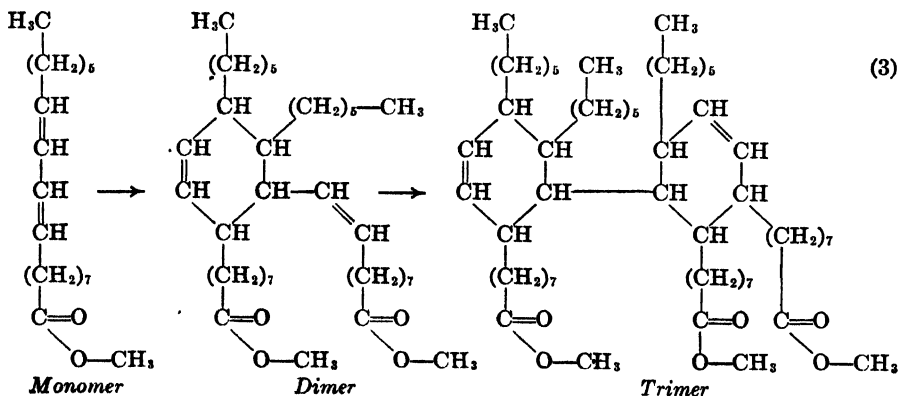
* Manufacturer's Data. The Resinous Products and Chemical Co.

Linear Polyesters of Medium to High Maleic Unsaturation. Unsaturated linear alkyds comprising glycol and polyglycol esters of maleic acid which possess medium to high unsaturation are not only convertible by heat, peroxides, and oxygen, but they can also be vulcanized with sulfur in much the same manner as rubber and are used to some extent in elastomeric compositions. The resulting vulcanizates are more resistant to the action of hydrocarbon solvents than natural rubber. These products do not stiffen with age. Sulfur vulcanizable "Paracons," like "Paraplex" S-200 belong to this category of alkyds.

Analogous polyesters are also capable of copolymerization with numerous unsaturated monomeric compounds such as vinyl acetate, styrene, and methyl methacrylate. Cross-linked, tridimensional resins are formed by copolymerization with these unsaturated monomers which apparently bridge the polyester chains. Plastics of this kind are discussed in greater detail in Chapter 19, under contact resins.

Linear Polyesters of Non-Maleic Unsaturation. *Polyesters from Dimerized Fatty Acids.* Certain unsaturated linear alkyds can be cross-linked by means of sulfur, assisted by the usual rubber accelerators. It has been noted in the preceding section that certain varieties of "Paracon" containing medium to high maleic unsaturation can be cured in this way. Other useful vulcanizable alkyds are derived from dimerized drying oil acids.

By methanolysis, drying oils can be converted to mixtures of the corresponding methyl esters. Where conjugated unsaturation exists in these methyl esters or where it can be induced by rearrangement of a non-conjugated system, they can be thermally polymerized to mixtures consisting largely of dimers and trimers. On the basis of various physical and chemical properties of fractions obtained by molecular distillation, this reaction has been tentatively formulated in the Diels-Alder sense as follows:



Reaction (3) can be brought about by heating for several hours at 300° in a carbon dioxide atmosphere. The more saturated unpolymerizable monomeric esters present in the products of methanolysis of drying oils are unaffected by this treatment and can be distilled off below 300° at 1 mm pressure. Dimers and trimers remain behind as a residue which can be distilled only in a molecular still. Various catalysts, such as anthraquinone, silico-tungstic acid, boron trifluoride, Floridin (a variety of Florida clay), and others, are of assistance in dimerizing methyl esters of drying oil acids.

Reactions of this category can be applied to soybean oil, linseed oil, tung oil, dehydrated castor oil and other drying oils.

Saponification of the dimerized methyl esters yields the corresponding dibasic acids. The latter can be esterified with glycol to yield unsaturated polyesters which are reactive with sulfur and can be vulcanized with the aid of ordinary rubber vulcanization accelerators. The initial polyester is soft and sticky and does not handle well on rubber rolls, but after partial curing with sulfur, most of the tack is lost, the product is solid, and it can be compounded on a mill with the usual rubber ingredients. Vulcanization can then be completed subsequently, yielding soft, elastic stocks which possess tensile strengths averaging 400–500 lbs/sq in and elongations averaging 100–130 per cent. They show good retention of elastic properties at sub-zero temperatures. These products are not resistant to petroleum solvents and oils, but are unaffected by alcohol and water. They are resistant to ozone. Their tensile strength is considerably less than that of rubber and their elongation not as good, either. For many mechanical applications such as packings and glass jar rings, however, these characteristics are quite good enough. For such uses they played a significant role during the rubber shortage. They were originally developed from soybean oil by the U. S. Northern Regional Laboratory and hence were named "Norepol." In close cooperation with the government laboratories several firms undertook manufacture of these rubber-like alkyds from various vegetable oils, the processes employed differing slightly from one firm to another, depending upon their past experience and "know-how." Current trade names for these materials include "Agripol," "Vulprene," "Sulprene," "Kem-pol," and "Witcogum."

Linear Polyesters Modified with Drying Oil Acids. It has been noted in an earlier section that linear polyesters containing maleic unsaturation can, like drying oils, be converted to insoluble, infusible products by oxidation, either with or without the aid of driers. Where modified with the acids of drying oils, these maleic polyesters are even more readily oxidized. It is significant that the latter products differ markedly in drying characteristics from corresponding modifications of linear polyesters of saturated

dibasic acids. For example, films of polyethylene maleate modified with linseed oil acids can be converted to light-colored hard surface coatings by brief stoving at 140°, or, more slowly, by air-drying at room temperature, with or without the aid of driers. Films of polyethylene succinate, adipate, or sebacate, on the other hand, modified with the same mole per cent of linseed oil acids, yield strongly discolored films—and then only with difficulty, from 10 to 14 hours' heating at 140° being required; they will not air-dry at room temperature.

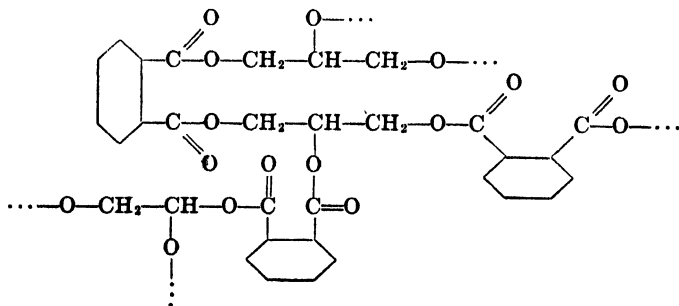
Polyesters of Polyfunctional Reactants

General

In 1944, American production of non-cellulosic synthetic resins reached a total of 784,000,000 pounds. Alkyds accounted for almost a third of this volume, or 245,000,000 pounds—the largest production of any single class. The rapid commercial development of alkyd resins during the past fifteen years has resulted from their introduction as vehicles for surface coatings. Numerous ramifications of this single application still account for the bulk of these materials.

Where either the acid or alcohol entering into formation of an alkyd resin is more than bifunctional, complex tridimensional polyesters are produced if reaction is carried to completion.

Glycerol and phthalic anhydride, for example, react at temperatures in the order of 160° or above to form a resinous product, liquid at that temperature, which gradually increases in viscosity as heating continues until gelation suddenly occurs. Upon cooling, the product is hard and brittle. The gelled resin is insoluble and infusible, in mass. It still contains some extractable, fusible components, however, the amount of which can be reduced by further heating. The initial gelled resin is thereby converted to a harder product. A segment of the cured resin may be represented as follows, although a limited number of secondary reactions occur which probably yield a more complicated material:



Most alkyds are not only constituted of polyfunctional acids and alcohols; they are also modified in diverse ways which will be discussed later. The majority of commercial resins of this class, however, regardless of modification, are capable of being cured to three-dimensional structures similar to that just illustrated. The use of these resins in surface coatings in general depends upon arresting reaction short of gelation, at which point the polyester can still be dissolved in suitable solvents, with or without drying oils and pigments, and applied, as a varnish or lacquer, to various surfaces from which the solvent is subsequently evaporated and upon which the residual resin is later set up by heat or oxidation to a cross-linked insoluble form.

The manufacture of alkyd resins is conducted under conditions which permit careful control of the ratio of reactants, temperature, uniformity of mix, and time of reaction. The cooking operation is carried out in aluminum or stainless steel kettles containing from one to several tons apiece, equipped with reflux condensers, agitators, and suitable means for sampling and discharge. Reactants are often weighed out on the floor above the kettles so that they can be transferred thereto by gravity. Circulating oil, Dowtherm, and electricity are the preferred methods of heating the vessels. In order to maintain light color, reaction should be carried out under an inert atmosphere; hence the kettles are connected with a source of carbon dioxide which may be bubbled through the mass. Some plants are equipped with vacuum which can be applied to the reactors.

Inasmuch as a considerable amount of heat is held by the viscous resin, it requires an appreciable time to cool from reaction temperature. In the manufacture of alkyds for surface coatings, esterification is usually carried just short of the point at which cross-linking would occur to yield a gelled mass. There is therefore danger that the retained heat will be sufficient to set the resin up to the gel stage before it cools. Hence it is common practice to cut it with an appropriate solvent, such as toluene, after heating has progressed far enough. This operation cools the mix sufficiently to stop further reaction. It is best conducted by running the hot alkyd into solvent held in a container equipped with a reflux. Although some alkyds are supplied as 100 per cent resin, the majority are cut with solvent and are customarily available in about 50 per cent solution. Use of solvent has two further advantages. It permits more ready clarification of the resin and it reduces the customer's loss from adherence of thick, 100 per cent resin to container walls.

Glycerol and phthalic anhydride are by far the most important fundamental components of commercial alkyds. Maleic anhydride is the second most valuable dibasic acid intermediate, although in the vast majority of

maleic alkyds, maleic anhydride is not used as such, but rather as its rosin adduct, as in certain "Amberol" resins. In 1943, about 154 million pounds of alkyds came from phthalic anhydride; about 25 million pounds from maleic anhydride.

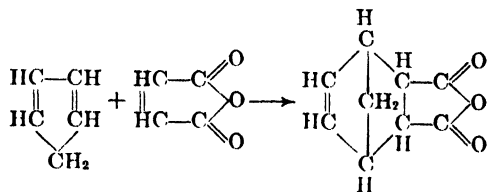
Alkyd resins, based for the most part on these three intermediates, and variously modified, are manufactured under numerous trade names, including "Amberlac," "Amberol," "Aquaplex" (aqueous emulsion), "Arochem," "Aroflex," "Aroplaz," "Beckacite," "Beckosol," "Dulux," "Duraplex," "Dyal," "Dymal," "Esterol," "Falkaloid," "Falkyd," "Glyptal," "Lewisol," "Makalot," "Mirasol," "Paranol," "Rauzone," "Rezyl," "Syn-tex," "Teglac," and others, some of which are mentioned below. It should be noted that some of these names, like "Makalot" and "Beckacite," are also applied to other types of resins, such as phenolics. Most of them designate a wide range of alkyds made by a given concern and modified in many different ways. Prices in 1944 averaged from 12 to 14 cents per pound in 50 per cent solution in the case of the more common products.

While glycerol, phthalic anhydride, and maleic anhydride are the principal polyfunctional intermediates for commercial alkyds, several other chemicals are used in much smaller volumes.

Other polyhydric alcohols include ethylene glycol, diethylene glycol, pentaerythritol, and sorbitol.

Other dibasic acids used to some extent are succinic, adipic, azelaic, and sebacic. Alkyds based upon sebacic acid are particularly well known. They find especial use as plasticizers for finishes based on other resins, including coatings for rubber and fabrics where they impart added resistance to abrasion and scuffing as well as durability and high flexibility. They are also used in special caulking compounds and adhesives. Sebacic acid alkyds are manufactured under the trade name "Paraplex."

A unique dibasic acid which has lately appeared is known as "Carbic" anhydride. It is produced by a Diels-Alder addition of maleic anhydride to cyclopentadiene:


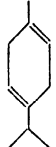



"Carbic" anhydride is used in the manufacture of the so-called "C-9" alkyds, apparently so-named because of the presence of nine carbon atoms in this intermediate.

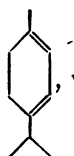
Another unusual dibasic acid used in alkyd resins has been manufac-

tured for several years under the trade-mark "Petrex" polybasic acid. Maleic anhydride, again, is reacted with diolefinic hydrocarbons—terpenes in this case. The product is a mixture of complex addition products.

Non-conjugated monocyclic terpenes possessing the *p*-cymene skeleton

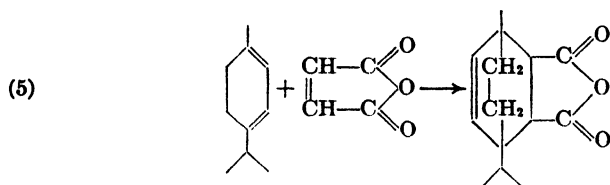
such as dipentene: , γ -terpinene: , and terpinolene: , isomerize

rapidly in the presence of either organic or inorganic acids to α -terpinene:

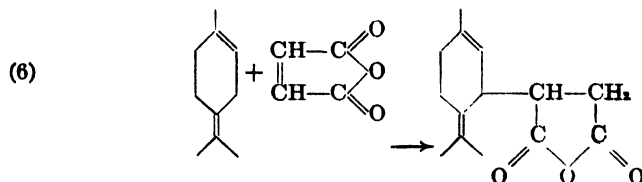


, which undergoes a Diels-Alder condensation with maleic anhydride

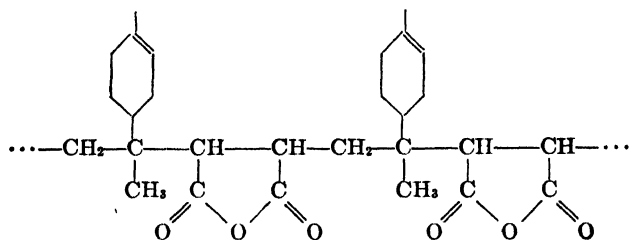
to give the anhydride of a complex dibasic acid as follows:



The presence of small amounts of maleic acid during reaction (5) is sufficient to cause isomerization of the non-conjugated terpenes of turpentine to α -terpinene, with consequent formation of the Diels-Alder adduct. Until lately, "Petrex" acid was considered to be this Diels-Alder addition product of maleic anhydride and α -terpinene. Recent work, however, seems to indicate that such is not the case. Approximately 50 per cent of "Petrex" polybasic acid is reported to be a non-Diels-Alder adduct of terpinolene and maleic anhydride, produced according to equation (6).



The remainder is a mixture of macromolecular polybasic acids of molecular weights ranging from 450 to 3000. The following formula has been tentatively proposed as representing a portion of these polybasic acids:



"Petrex" polybasic acid is a component of the "Petrex" alkyds.

The "Petrexes" possess better solubility in cheap solvents than do most other alkyds, because of their terpenic character. They are premium priced resins which have found especial application in roller coating enamels, tin decorating finishes, and heat sealing paper and textile coatings. They can be used for bonding applications with metal foils and cellophane. They exhibit unusually good flowing and levelling characteristics. They are priced at about 40 cents per pound.

Unmodified or Straight Tridimensional Alkyds

It has been shown that glycerol and phthalic anhydride react with each other at elevated temperatures to form polycesters. During the early stages of resinification the hot reaction mixture is liquid. Upon continued heating more complete esterification occurs, resulting in a cross-linked gel which forms rapidly throughout the entire mass, once it appears. The tridimensional structure thus created is hard and brittle upon cooling and is insoluble in most solvents. Long-continued heating of the gel converts it to a still harder, more insoluble product in which brittleness gives way to toughness. The probable formula for a typical section of a gelled glyceryl phthalate resin was shown on page 236.

As in the reaction of phthalic anhydride with ethylene glycol, esterification under isothermal conditions is about half over within the first minute at 190°. Gelation, however, occurs before esterification is complete, usually at 75–79 per cent reaction. The log of the gelling time is a linear function of the reciprocal of the absolute temperature of reaction, as shown in Figure 94. Figure 95 shows the relationships between free acidity, evolved water, and time of esterification of glycerol and phthalic acid under a given set of conditions.

The initial gelled resinous product begins to soften at temperatures above 40°, but does not melt below its decomposition point. It is slowly attacked by water and, upon prolonged exposure, whitens and softens. On long heating, condensation is carried further to a point where the resin is far more resistant to water. Both the final and intermediate products of resinification are insoluble in the usual organic solvents. Although not

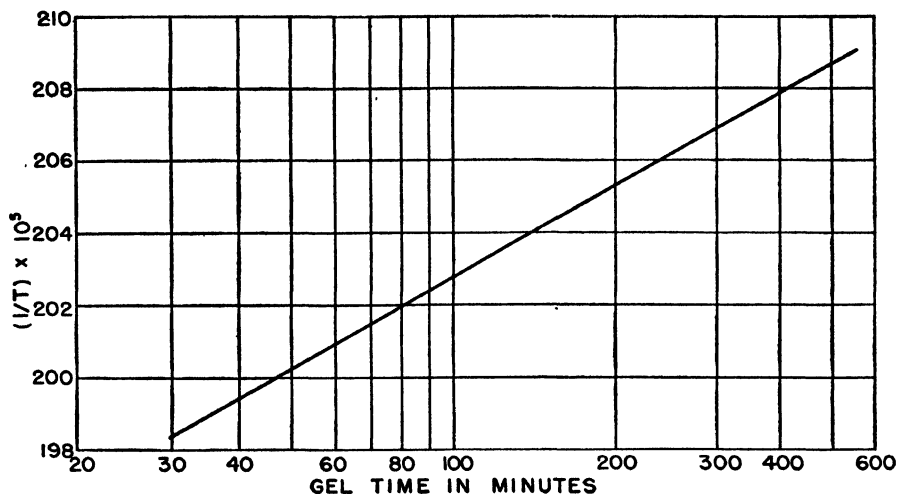


Figure 94. Gel time *vs.* reciprocal of the absolute temperature in the esterification of glycerol with phthalic anhydride in 2:3 molar ratio. (Kienle and Hovey³⁵)

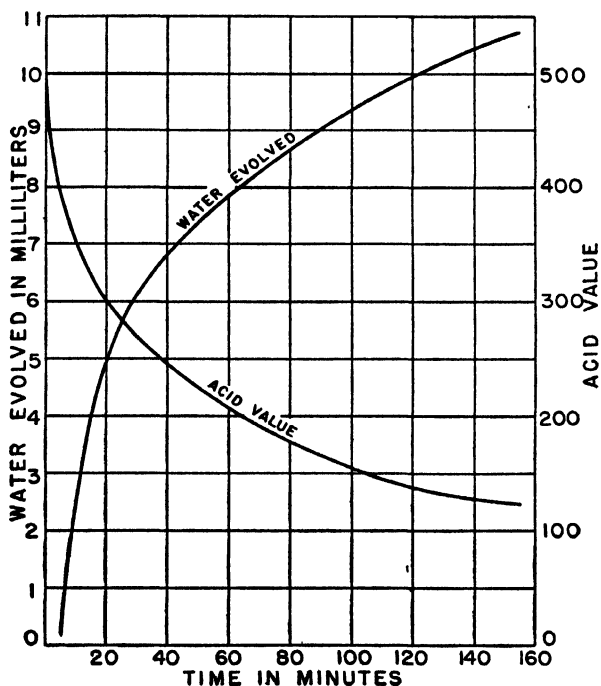


Figure 95. Relation between time of reaction, evolution of water during condensation, and acid number of the product formed by esterification of glycerol with phthalic acid in 2:3 molar ratio at 190°. (Kienle, van der Meulen, and Petke³⁶)

truly soluble in glycerol, they react with it, degelling by ester interchange. If reaction be carried out in an atmosphere of carbon dioxide, or *in vacuo*, the product is almost colorless.

In accordance with the nomenclature adopted for the phenolics, heat-convertible alkyds have been classified as A-, B-, and C-stage resins, depending upon the extent of resinification as reflected by their resistance to acetone and cold water. A-stage alkyds are fusible and soluble in acetone, hence clearly distinguishable as pre-gel resins. The line of division between B and C stages is much less clean-cut.



Courtesy The Resinous Products & Chemical Co.

Figure 96. In the production of "Paraplex" resins, the filter press is used to remove any impurities which might affect their uniformity.

Both B- and C-stage resins can be molded, but usually with much difficulty. Prolonged heating is required. Moreover, decomposition attended by gas formation often occurs where alkyds are molded under pressure. Hence, in commercial practice, molding powders of alkyd resins are not manufactured and molded alkyds are very limited in number.

Straight glyceryl phthalates have not been widely used industrially because of their restricted solubility relationships. Nevertheless, the first technical application, still important, of alkyds was the use of A-stage glyceryl phthalate in acetone solution as a bonding agent for mica. After evaporation of the solvent, the coated mica is molded under pressure while the resin is heat-cured. Oil-modification is used in the production of flexible mica sheet.

Many other dibasic acids besides phthalic have been used in the manu-

facture of straight tridimensional alkyds. Resinous glycerol esters of both phthalic and maleic acids are hard and brittle at room temperature. Those produced from polymethylene dicarboxylic acids, on the other hand, are more or less flexible. Their softness and flexibility increases as the chain length mounts from succinic to sebacic acid. Glyceryl sebacates are soft and pliable.

The characteristics of various heat-convertible alkyds are given in Tables 26 and 27.

Table 26. Effect of Varying Reactivity of Acid in Heat-Convertible Alkyd Resins ³³

Acid	Reactivity of Acid	Reactivity of Alcohol (glycerol)	Flow Point * of Resin (° C)	Remarks
Benzoic	1	3	—	Simple esters; no resin
Phthalic	2	3	110–115	Hard, glassy, clear
Acetic	1	3	—	Simple esters; no resin
Succinic	2	3	—	Medium hard, flexible
Citric	3	3	60–80	Hard, brittle resin
Maleic	3	3	90–100	Hard, tough resin

* Taken just prior to conversion.

Table 27. Effect of Varying Reactivity of Alcohol in Alkyd Resins ³³

Alcohol	Reactivity of Acid (phthalic)	Reactivity of Alcohol	Type of Resin	Flow Point * of Resin (° C)	Water Resistance	Remarks
Methyl	2	1	—	—	Insoluble	No resin, pure compound
Ethylene glycol	2	2	Heat non-convertible	80–85	Excellent	Hard, glassy resin
Propylene glycol	2	2	Heat non-convertible	70–80	Excellent	Hard resin
Diethylene glycol	2	2	Heat non-convertible	20	Excellent	Balsam
Glycerol	2	3	Heat-convertible	110–115*	Fair	Hard, glassy resin
Mannitol	2	6	Heat-convertible	117*	Poor	Hard, opaque resin

* Flow point taken just prior to conversion.

The properties of cross-linked alkyds can be modified by admixing several polyfunctional reactants. Thus, by reacting phthalic anhydride, glycerol, a glycol, and a saturated aliphatic dibasic acid such as succinic, adipic, or sebacic acid, cured C-stage resins are obtained which are flexible and possess more or less rubber-like qualities. The degree of flexibility and softness increases as the proportion of bifunctional reactants is increased. To some extent, flexibility is also augmented as the length of the polymethylene chain of either the glycol or aliphatic acid is increased. Resins of this category can be cast before gelation and then cured, or they

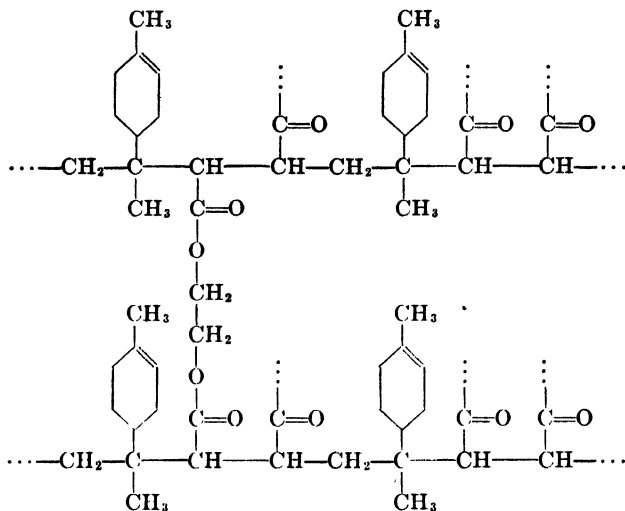
can be cured to the B- or C-stage, then milled on rubber rolls, compounded with fillers or other materials such as rubber or a synthetic rubber, and further cured at temperatures of 125° or above. Table 28 gives a comparison of a series of products prepared from glycerol, ethylene glycol, phthalic anhydride, and succinic acid.

Table 28. Comparison of Certain Physical Properties of a Cured, Flexible Resin Series²⁸

Molar Ratio of Glycol Succinate to Glyceryl Phthalate in Resin	Cast Sheets		Plastic Sheets		Remarks
	Shore Hardness	Shore Elasticity	Shore Hardness	Shore Elasticity	
1 : 1	99	—	100	—	Very tough, stiff, hard
2 : 1	97	—	100	—	Tough, hard, bendable
4 : 1	95	33	100	—	Tough, flexible
6 : 1	83	38	74	43	Tough, very flexible
8 : 1	63	95	49	88	Rubbery, exceedingly flexible
10 : 1	55	95	39	95	Very rubbery

Flexible alkyds of the kind just described often show a tendency to de-gel and become sticky on prolonged standing at room temperature. This fact has militated against their general application. They are, however, manufactured in limited amounts. "Glyptal" 1253-U, for example, appears to be the reaction product of glycerol, ethylene glycol, phthalic anhydride, and adipic acid. This, or an analogous product appears to be used to some extent in combination with neoprene in the manufacture of "Vulcan" offset printing blankets. The attempted use of this type of composition as a leather substitute in gas meter diaphragms is said to have been somewhat less successful.

A different type of flexible alkyd has been developed by Hercules Powder Company from the polybasic acid component of "Petrex" shown on p. 240. Three-dimensional alkyd resins can be prepared from either the dibasic or polybasic acid components of this product by esterification with glycerol or other polyhydric alcohols and such alkyds are available in certain numbered grades of "Petrex" resins. Esterification of the dibasic acid component of "Petrex" with ethylene glycol yields only a linear, thermoplastic polyester. Inasmuch as about half of the complex terpene-maleic anhydride reaction product consists of the above-noted resinous polybasic acid, however, esterification of the entire acid mixture with glycol produces a three-dimensional resin, self-plasticized with the linear alkyd just mentioned. A portion of the cross-linked resin produced with ethylene glycol may be represented as follows:



Both glycerol and ethylene glycol polyesters of "Petrex" polybasic acid are hard, brittle solids. Diethylene glycol yields a tough, somewhat elastomeric product, while triethylene glycol gives a still softer polyester, tough, flexible, and rubber-like. The hexaethylene glycol resin gels with difficulty. The nonaethylene glycol ester is a soft, non-gelling balsamic fluid at room temperature.

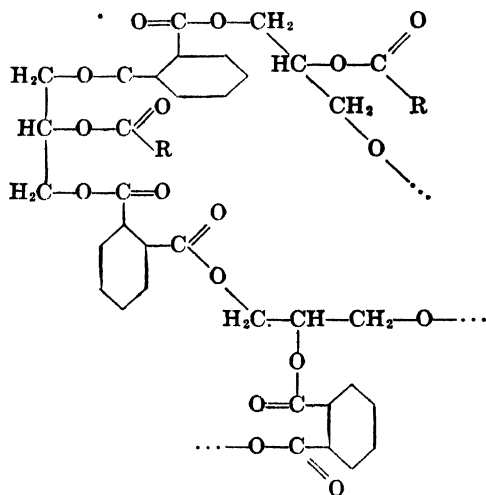
Non-Drying Oil Modified Tridimensional Alkyds

It has been remarked that the bulk of commercial alkyds today are modified with one or more of several different types of materials. This is almost universally true in the case of resins destined for surface coatings, the straight alkyds previously discussed having limited specialty uses, but almost none at all as varnish or lacquer vehicles, although some of them may be used therein as plasticizers.

A portion of the dibasic acid used as an intermediate in alkyd resin formation can be replaced by an equivalent amount of a monobasic acid. Likewise, a portion of the polyhydric alcohol employed can be substituted by a monohydric alcohol. The properties of the product will be modified accordingly. In actual practice, monohydric alcohols are scarcely ever utilized. Monobasic acids, however, are very important. The use of volatile fatty acids appears to have no special merit. On the other hand, incorporation of the higher fatty acids—non-drying, semi-drying, or drying—into the structure of alkyds yields products which are more flexible than the corresponding unmodified resins. They are also more compatible with other resins, notably cellulose nitrate, ethyl cellulose, and

chlorinated rubber, and improve flexibility and adhesion of the latter resins. From 25 to 80 per cent of the resin may be fatty acid. Short oil lengths possess from 25 to 50 per cent of fatty acids, medium oil lengths from 50 to 65 per cent, while long oil alkyds may have as much as 80 per cent of fatty acids in their structure. In this section we shall confine our attention to alkyds modified with non-drying oil acids.

These resins can be cured by heat to tridimensional, insoluble structures, a portion of which may be typified as follows:



where R represents the residue of a fatty acid.

The principal non-drying and semi-drying oils employed in the modification of alkyds are coconut oil, cottonseed oil, and castor oil. In preparing these resins, the oils themselves, with the exception of castor oil, are not reacted directly with phthalic anhydride and glycerol, or other components, for they are immiscible therewith and reaction is so slow that the anhydride and glycerol react together and gel before the oil enters into the structure of the resin. The oil, however, may first be converted to monoglycerides by heating with glycerol before addition of the acid anhydride. Reaction then occurs as desired. This method is used in the manufacture of a very considerable proportion of alkyds because of its relatively low cost in comparison with other processes. In view of the fact that purified, distilled fatty acids have become increasingly available in recent years, however, it is now also fairly common practice to react the free fatty acids with glycerol and phthalic anhydride directly.

Reaction is stopped before gelation occurs and the resins are cured by heat after application to the surface to be coated. One of the main uses

of non-drying alkyds is in combination with urea-formaldehyde resins in baking finishes. These non-drying alkyds are also used in the A-stage as permanent plasticizers for nitrocellulose or other air-dried lacquers.

Oil modified alkyds are more soluble in hydrocarbons and other solvents than the corresponding unmodified resins. Their solubility increases with increasing oil length. Where the degree of modification reaches 50 per cent, the resins are quite soluble in petroleum solvents. Straight glyceryl phthalates, on the other hand, are insoluble in both aliphatic and aromatic hydrocarbons. Non-drying alkyds are usually modified to the extent of 25 to 40 per cent. They are, therefore, relatively poor in petroleum solvency as a rule and require coal tar hydrocarbons, esters, chlorinated hydrocarbons, or lower ketones to produce satisfactory solutions. Alcohols may be used to effect reduction of the viscosity of these solutions.

Non-drying oil modified alkyds are utilized in coatings for linoleum, leather, fabrics, and rubber, often in conjunction with other resins. High grade artificial leather, for example, is produced by coating fabric with semi- or non-drying oil modified alkyds admixed with nitrocellulose. Other uses include clear metal lacquers for both interior and exterior service. They are particularly important as plasticizers for nitrocellulose in automobile lacquers where they may be used in amounts varying from equal quantities to twice as much alkyd as cellulose ester. Other resins plasticized with this class of alkyd include urea-formaldehydes, especially, and ethyl cellulose, chlorinated rubber, melamine, and drying oil-modified alkyds. Non-resinous plasticizers are sometimes used in conjunction with non-drying oil-modified alkyds of medium or short oil length where the latter are combined with other synthetic or semi-synthetic resins.

Drying Oil Modified Alkyds

Incorporation of the acids of drying oils into the molecular structure of an alkyd seems an obvious step from the use of non-drying oil acids, yet more than ten years elapsed between these two developments. This time lag is in part explicable by the limited knowledge of macro-molecular substances then existing. The utilization of drying oil acids represented a great advance because the resulting alkyds not only possess solubility characteristics similar to those of the non-drying oil alkyds, but they also yield hard films by either baking or air-drying. Indeed they air-dry much more rapidly than the oils from which they are prepared. The dried films are tough and durable, weather well, and possess high gloss, excellent adhesion to metallic surfaces, and superior resistance to light, heat, and chemicals. Baked-on films show better water resistance than those formed by air-drying. Baking temperatures vary from 150° F to over 300° F, depending on conditions.

The most important drying oils used to modify alkyds are soybean, linseed, dehydrated castor, tung, fish, perilla, and oiticica. Others include sunflower and walnut oils. Drying is much more rapid than with the oils themselves and is usually in the same relative order as the unreacted oils. Although alkyds modified with soybean oil are slower drying than those prepared from linseed or dehydrated castor oils, and much slower than tung oil modified resins, nevertheless soybean oil is an excellent



Figure 97. Phthalic anhydride, glycerol, and oil acids are reacted together to form "Duraplex" alkyd resins.

*Courtesy The Resinous Products
& Chemical Co.*

modifier, giving light-colored, rapid-drying alkyd resin varnishes. Tung oil, however, although a superior drying oil by itself, is not very satisfactory as a modifier for alkyds because it is so reactive that well condensed, low acid number resins can be prepared from it only with difficulty.

In general, the greater the oil length, the longer the time required for a drying oil modified alkyd to set and harden, although complete hardness *throughout* the film develops more rapidly with increasing oil length. Flexibility and water-resistance increase with oil length. Mineral spirits tolerance of the alkyd also improves with the amount of oil modifier; this characteristic is reflected in increasing ease of brushing and compatibility with oils and varnishes, but in decreasing resistance of the dried film to

oil and gasoline. Air-dried long oil alkyds possess somewhat better durability than the corresponding short oil resins, but the reverse is true of baked-on films. Hardness, mar-resistance, gloss, and color retention of short oil modified alkyds are also better than in the case of long oil resins where the films are cured by baking.

Drying oil modified alkyds are used both alone and admixed with other resins like cellulose nitrate, ethyl cellulose, and chlorinated rubber. The latter improves drying speed, but may adversely affect adhesion.

Hovey has listed various general methods of blending alkyds with other materials commonly used in adhesive formulation as shown in Table 29.

Table 29. Methods of Blending Alkyds with Other Adhesive Materials ³¹

Material	Method of Blending with Alkyd Resins
Mastic	1,2,3,4
Dammar	1,2,3,4
Rosin	1,2,3,4
Shellac	3,4
Copal	1,3
Rubber (smoked sheet)	1,3,4 if with a hydrocarbon- soluble resin
Water glass	5
Glue	3,5
Pitches	3,4 if resin is of hydrocarbon- soluble type
Casein	3,5
Chicle	3,4
Rubber latex	3,5
Nitrocellulose	3,4
Pine tar	1,2,3,4
Canada balsam	1,2,3,4
Drying oils	1,2,3,4,5
Phenolic resin	1,3,4
Urea resin	1,3,5
Polyvinyl acetate	3,4
Coumarone resin	1,2,3,4

1. Cooking with other ingredients in preparation of alkyd resin.
2. Simple heat-blending.
3. Hot mixing on rolls, in dough mixer, or in Banbury.
4. Dissolving both in a common solvent or in miscible solvents.
5. Using a water solution of ammonia or triethanolamine.

Drying is facilitated by addition of conventional driers such as lead, cobalt, manganese, and zinc fatty acid salts, naphthenates, or resinates. The amounts used generally range from 0.01 to 0.5 per cent metal, based on resin content, the exact quantity depending on the nature of the resin, drier, and drier combination. The use of zinc drier helps to prevent wrinkling.

The formulation of paints, varnishes, lacquers, and enamels based on

alkyd resins is as much of an art as the preparation of these materials with any other type of vehicle. The alkyds are used in solution in organic solvents which are customarily thinned with coal tar or petroleum naphthas. They are also employed in solution in drying oil vehicles such as tung, linseed, oiticica, perilla, and dehydrated castor oils. Long-oil alkyds blend best with drying oils. Care must be exercised to ascertain that initially homogeneous blends do not tend to separate on standing. Short oil varnishes in which the oils have not been subjected to excessive heat treatment are most satisfactory for blending with alkyds.

Less commonly, alkyds are applied from aqueous emulsions.

Pigmentation must be carried out with care. During the early years of the alkyds, the high acid numbers frequently encountered prevented use of reactive basic pigments. These materials should still be used with caution, although manufacturing control has advanced greatly during the past decade so that many resins are now available which possess such low acidity that they can be combined with practically all common pigments, including zinc oxide. Acid numbers of commercial resins usually run from about 3 to 60, although they may occasionally be either higher or lower than this range.

In typical white enamels, approximately equal parts of pigment and alkyd resin may be employed. With organic reds, from 3 to 6 times as much resin as pigment may be used, while with carbon black the ratio of resin to pigment may run as high as 15 or 20 to 1. In primers, the amount of pigment may be in excess of the resin—often from 2 to 4 times as much.

Particularly satisfactory flattening of alkyd finishes can be accomplished by the use of fine diatomaceous earth.

Typical formulations of drying oil modified alkyds are given on the following page as recommended by the manufacturer of the resins involved.

Resins modified with drying oils are the most widely used type of alkyd. Motor car, truck, and railway primers and finishes represent a very important outlet for these materials. They are also used on metal surfaces in numerous other applications, such as bridges, busses, bicycles, street cars, tank cars, lawn furniture, metal cabinets and housings, hardware, can coatings, signs, gasoline pumps, washing machines and other equipment for household, farm, and factory. They are utilized in arc-proof coatings for electrical parts including controller shafts, finger blocks, switch bases, armature coils, and frames, as well as in enamelled wire coatings. They are used in house paints, marine paints, and printing inks. For these last three applications long oil resins are usually employed whereas shorter lengths are used as vehicles for metal primers and metal finishes to be baked at low temperatures. Drying oil modified alkyds are

"Duraplex" C-45 HV Varnish Blend Red Enamel**Paste**

28% Toluidine Red
 58% "Duraplex" C-45 HV (60%)
 14% Mineral thinner

Enamel

100 parts Paste
 82 parts "Duraplex" C-45 HV (60%)
 56 parts F-0903 Varnish *
 54 parts "Troluoil"
 6 parts Xylene
 0.05% Cobalt
 0.025% Manganese
 0.5% Lead

} Drier based on resin solids

Enamel contains:

20% Pigment-Toluidine Red
 80% Resin solids { 3 parts "Duraplex" C-45 HV
 1 part Varnish

*** "Amberol" F-0903 Varnish:**

100 lbs "Amberol" F-7
 9 gal Tung oil
 3 gal Linseed oil (alkali refined)
 20 gal Mineral thinner
 Heat oil and resin to 585° F. Cool and reduce.

"Duraplex" C-45 HV is the trade name of an alkyd produced by the Resinous Products and Chemical Co. containing 33 per cent phthalic anhydride and modified with 56 per cent drying oil acids. Its acid number runs from 3 to 9. It is supplied as a 60 per cent solution in mineral spirits.

"Duraplex" C-49—"Parlon" White Enamel**Paste**

60% Pigment { 9 parts titanium dioxide LOCR
 1 part zinc oxide
 40% "Duraplex" C-49 (60% solids in Solvesso No. 2)

Enamel

100 parts paste
 35 parts "Duraplex" C-49 (60% solids in Solvesso No. 2)
 37.5 parts 10 cps "Parlon" (chlorinated rubber) (40% solids in xylene)
 10 parts Solvesso No. 2
 0.03% cobalt
 0.02% manganese

} based on "Duraplex" resin solids

Enamel contains:

50% pigment
 50% binder { 3 parts "Duraplex" C-49 solids
 1 part "Parlon"

Reduce 4 : 3 with xylene to spray.

Bake at 175-180° F for 30 minutes.

"Duraplex" C-49, also made by the Resinous Products and Chemical Co., contains 32 per cent phthalic anhydride. It is modified with 58 per cent drying oil acids (non-yellowing, probably soybean). Its acid number is 1 to 4, and it is supplied in 60 per cent solution in mineral spirits.

used in finishes applied to all manner of military equipment, from tanks and planes to battleships, anti-aircraft guns, and steel runway planks for airfields. Both drying and non-drying oil modified alkyds are used in flexible fabric coatings which exhibit particularly good resistance to mustard gas.

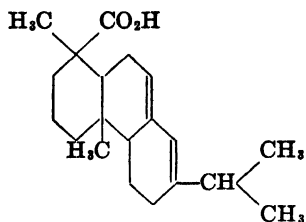
Before World War II, drying oil modified alkyds had gained general recognition for interior finishing in glossy rapid-drying lacquers. Military applications have emphasized flatted coatings. Their use in exterior house paints has lagged largely because of solvent cost, but it appears that this market is likely to become important, especially as a result of the introduction of aqueous emulsions of drying oil alkyds. Such emulsions can be purchased in concentrated form, then diluted with water and brushed or sprayed. Upon evaporation of the water, the resin globules coalesce into a coherent film which, upon drying, is impervious to water and can serve as a durable exterior as well as interior finish.

Alkyd resin emulsions can be applied to porous moist surfaces if necessary, such as plaster, stucco, wood, brick, or concrete. They have found especial favor in traffic and zone marking paints where they can be used without fear of bleeding of the asphalt road covering. They have gained military acceptance, being extensively employed in camouflage paints. In washability and weather resistance, alkyd resin emulsion paints are better than other types of emulsions. They are available under certain special trade names such as "Aquaplex" and as water emulsions of many trade products already listed such as "Beckasol," "C-9," and "Petrex."

Rosin-Modified Alkyds

Alkyd resins may be modified with rosin (abietic acid), or other natural resin acids. Rosin is the most common modifier, but ester gum and run copals are also used. The products are hard and brittle, soluble in many organic solvents, and compatible with drying oils and nitrocellulose. They are relatively high melting and exhibit excellent solvent release. Inasmuch as coatings containing these resins are considerably more brittle than those based on oil-modified alkyds, they do not weather as well as the latter and possess poorer durability. Alkyds modified with rosin may also be modified with either drying or non-drying oil acids.

Rosin is especially favored as a modifier for alkyds prepared from maleic anhydride. The rosin may be added directly with the other resin intermediates, or it may first be reacted with maleic anhydride to form an addition product which is then resinified by esterification. The main constituent of rosin is a triterpenic compound, abietic acid. L. Ruzicka and his school, especially, have studied the structure of this acid which is represented as shown at the top of the next page. Because it is



thought to possess conjugated unsaturation, it may be that this intermediate rosin-maleic anhydride adduct is the result of a Diels-Alder synthesis. This possibility, however, has by no means been proved and in view of the diversity of reactions into which maleic anhydride can enter with unsaturated systems—as typified by the earlier discussion of “Petrex” polybasic acid—no certain statement concerning the structure of this addition product can as yet be made.

Rosin-modified alkyds are especially favored in lacquer sanding sealers. They are used in 4-hour enamels and in varnishes for general interior application, for furniture and radio finishing, and for hardware protection where external weathering will not be encountered. They are used for decorating tinware and in collapsible tube enamels, in linoleum varnishes, and in printing ink formulation.

Typical rosin-modified alkyds include “Amberol” 800, 801, 801-P, and 806-P; “Beckacite” 1111 and 1120; “Lewisol” 2L, 28, and 33; “Petrex” No. 1, and variously numbered “Teglacs.”

Synthetic Resin Modified Alkyds

It is common practice to modify alkyd resins with other synthetic and semi-synthetic resins. In some instances, this amounts merely to a physical combination, based upon compatibility, as in the use of oil-modified alkyds in conjunction with cellulose nitrate, ethyl cellulose, and chlorinated rubber. Such mixtures are usually prepared by the varnish or lacquer formulator. In other cases, some sort of chemical combination occurs and the modifying resin may be combined with the alkyd before it reaches the formulator. This situation is particularly true of modifications with phenolic and urea resins where combination presumably occurs through the etherification of methylol groups present in A- or B-stage formaldehyde condensation products of these two types.

Phenolic Modified Alkyds. In the case of modification with phenolics, the cured film is harder and more resistant to water, chemicals, and heat than the alkyd itself. It is usually quicker setting, shows higher gloss, and possesses better water-resistance, where air-dried, than the alkyd alone. On the other hand, its initial color as well as its color retention is usually not as good as that of the alkyd. By way of contrast, the

color of the corresponding phenolic resin, itself, is improved. Its adhesion is bettered. Its flexibility is likewise augmented.

Phenolic resin modified alkyds may also be modified with oils and with natural resins.

These resins find typical uses on metal furniture, farm and factory machinery and tools, motor car accessories, washing machines, molded plastic parts and, where modified with oils, in traffic and zone marking paints.

Urea and Melamine Modified Alkyds. Alkyds are also modified with urea and melamine resins. The latter are utilized in an intermediate stage of condensation, often in the form of half acetals produced by reaction with lower aliphatic alcohols such as butanol. In such surface coatings, color and color retention of the alkyd is improved and hardness is increased. In the case of melamine modifications, hardness is especially pronounced so that care must be exercised to retain sufficient flexibility to prevent the film from chipping because of brittleness. In water and heat resistance, melamine modifications show superiority over those of urea. Such resins are also modified with oils.

Urea-modified alkyds are employed especially where white or light colored coatings possessing excellent color retention are essential, as in refrigerators and bathroom and hospital equipment.

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Chapter 12

Polyamides — Nylon

History

Nylon is a generic word coined in 1938 by the du Pont Company to designate a whole family of new products—the synthetic polymeric amides. It is not a trade-mark. Du Pont's official definition for nylon is as follows:

"A generic term for any long-chain synthetic polymeric amide which has recurring amide groups as an integral part of the main polymer chain, and which is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis."

Because of certain similarities between nylon and natural fiber proteins, it has occasionally been said that the former had its inception in earlier scientific work on the nature of proteins. This idea, however, is rather stretching the imagination. It is quite true that, long before nylon, Emil Fischer and others had recognized proteins as being constituted of various α -amino acids. Certain synthetic condensation products of these acids had been prepared and, indeed, a few products—some of which were thought to be polymers—had even been made from dibasic acids and diamines, an example being polytetramethylene carbonamide. Fiber-forming characteristics of these polyamides, however, were not noted. Descriptions were sketchy and of little merit and the products themselves possessed no known or contemplated utility. The existence of amido groupings in proteinaceous substances and in animal fibers was thus well recognized at the time that the development of nylon was begun, and indeed, other du Pont research had been directed toward improved types of fibers based on amino derivatives of cellulose, from which no commercially suitable fiber resulted. Nevertheless, nylon was not the result of any of this previous work. It was rather an outgrowth of fundamental studies on the nature of polymerization which began with an investigation of linear polyesters. Some of this work has been described in Chapter 11.

In 1928 the du Pont Company began a program of fundamental research in their Chemical Department at the Experimental Station in Wilmington and employed W. H. Carothers to initiate and direct the organic chemistry group organized as part of this new activity. The broad aspects of polymerization and condensation formed the main theme of research and resulted in highly significant contributions to this field. These studies

included the investigation of various polymeric hydrocarbons, chlorinated hydrocarbons, alcohols, oxides, acid anhydrides, esters, and amides.

In their study of polyesters, Carothers and an associate, J. W. Hill, employed the molecular still as a means of continuing esterification beyond the point at which it normally stops under atmospheric pressure. By so doing they evolved superpolymers possessing molecular weights in excess of 10,000. Upon removing one of these superpolyesters from a still, Hill discovered that it could be drawn out into filaments from a molten mass of material and these filaments could, in turn, be cold-drawn still further under slight tension, thus permanently increasing their length by several times. Strength and toughness of the filaments were increased by cold-stretching; brittleness was decreased. The superpolyesters which were obtained in this early work, and with which these phenomena were first observed, softened at too low temperatures and possessed too great solubility in dry-cleaning fluids, for example, to yield suitable commercial fibers. Nevertheless, the invention of a method for producing linear superpolyesters and the discovery of their adaptability to cold-drawing, constituted the groundwork upon which nylon was later developed.

During the first three years of fundamental investigations in the du Pont Chemical Department at the Experimental Station, Carothers and Berchet had studied polyamides from ϵ -amino caproic acid and Carothers and Kirby had prepared a number of polyamides from dibasic acids and diamines. These products were less soluble and possessed higher melting points than the analogous polyesters.

Later, work was concentrated on the synthesis of a polyamide which might form the basis for a commercial textile fiber. On February 28, 1935, the superpolymer that was subsequently selected for commercialization was synthesized from hexamethylenediamine and adipic acid. By the following year responsibility for the commercial development of fibers from this "Polymer 66," so named because of the presence of six carbon atoms in each of its components, was assumed by the Rayon Department of du Pont. Rapid commercialization followed. The first pair of stockings was made in February, 1937, from yarn produced at the Experimental Station. A pilot plant was constructed during the summer of the following year and, in the fall of 1938, "Polymer 66" made its public debut in the bristles of "Dr. West's Miracle Tuft" toothbrush, under the trade-mark "Exton." In October, 1938, after a decade of intensive research and development, nylon was formally announced to the public. A year later, to the month, retail sale of nylon stockings, produced from pilot plant yarn, began on a trial basis in Wilmington. The first large-scale plant constructed at Seaford, Delaware, began operation two months afterwards. Nylon hosiery was placed on sale in all principal cities of the country on

the same day, May 15, 1940. So great had been the emphasis laid upon coal, air, and water as the sources of these new stockings that according to the *New Yorker*, an early shopper requested a pair produced from anthracite because she felt they ought to wear longer than those made of soft coal!

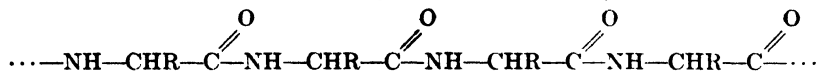
About 64 million pairs of ladies' stockings were sold during the first year. In 1941, between 17 and 20 per cent of all full-fashioned hosiery was knitted from nylon.

The Seaford plant was rapidly expanded to permit manufacture of about three times the amount of nylon originally intended. A second plant was soon completed so that production had again been doubled by the time that war broke out. Still further increases were made during World War II for military reasons.

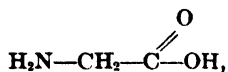
Numerous uses have been made of nylon in many forms during its brief and meteoric career. Throughout World War II, it was utilized almost exclusively for military purposes, among which parachute cloth was the most important. This application was formerly filled satisfactorily only by Japanese silk.

Chemistry

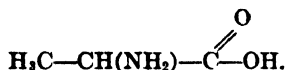
The structure of natural fiber proteins can be represented as follows:



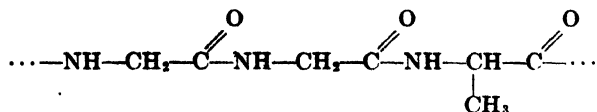
in which R may be any of several different radicals, usually more than one. The major components of silk fibroin, for example, are glycine,



and alanine,



These two α -amino acids are present in silk to the extent of about 40 per cent and 23 per cent, respectively, so that a portion of the structure of fibroin, neglecting less important constituents, can be depicted approximately as follows:



Wool protein is still more complex, R in the preceding general formula representing at least fourteen different groups corresponding to various amino acids which are present in this protein in the following proportions:

Amino Acid	Formula	Per Cent
<i>Glycine</i>	$\text{H}_2\text{N}-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$	0.6
<i>Alanine</i>	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH} \\ \\ \text{NH}_2 \end{array}$	4.4
<i>Valine</i>	$\begin{array}{c} (\text{H}_3\text{C})_2\text{CH}-\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH} \\ \\ \text{NH}_2 \end{array}$	2.8
<i>Leucine</i>	$\begin{array}{c} (\text{H}_3\text{C})_2\text{CH}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	11.5
<i>Serine</i>	$\begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	2.9
<i>Proline</i>	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \quad \diagup \\ \text{H}_2\text{C}-\text{CH} \quad \text{NH} \\ \\ \text{CO}_2\text{H} \end{array}$	4.4
<i>Aspartic acid</i>	$\begin{array}{c} \text{HO}_2\text{C}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	2.3
<i>Glutamic acid</i>	$\begin{array}{c} \text{HO}_2\text{C}-(\text{CH}_2)_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	12.9
<i>Cystine</i>	$\begin{array}{c} \text{HS}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	13.1
<i>Tyrosine</i>	$\begin{array}{c} \text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	4.8
<i>Tryptophane</i>	$\begin{array}{c} \text{Indole ring}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	1.8
<i>Arginine</i>	$\begin{array}{c} \text{HN}=\text{C}-\text{NH}-(\text{CH}_2)_3-\text{CH}-\text{CO}_2\text{H} \\ \qquad \qquad \\ \text{NH}_2 \qquad \qquad \text{NH}_2 \end{array}$	10.2
<i>Histidine</i>	$\begin{array}{c} \text{CH} \\ / \quad \backslash \\ \text{NH} \quad \text{N} \\ \quad \quad \\ \text{CH}=\text{C}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	6.9
<i>Lysine</i>	$\begin{array}{c} \text{NH}_2-(\text{CH}_2)_4-\text{CH}-\text{CO}_2\text{H} \\ \\ \text{NH}_2 \end{array}$	2.8
Total		81.4

These natural fibers are polyamides derived from α -amino acids.

Synthetic polyamides, designated nylons, are prepared either by self-condensation of various amino acids or by amidation of dibasic acids with diamines. The earliest superpolyamide to be made in the du Pont laboratories appears to have been that derived from ϵ -amino caproic acid, $\text{NH}_2-(\text{CH}_2)_5-\text{CO}_2\text{H}$. When this material was first prepared, difficulty was experienced in spinning fibers because of the refractory nature of the polymer. Attention was later directed to polymeric products derived from dibasic acids and primary or secondary (preferably primary) diamines, usually of aliphatic nature.

Upon neutralization of dibasic acids with diamines under mild conditions as, for instance, in aqueous or aqueous alcoholic solution, ionizable salts, often called nylon salts, are obtained which are constituted of molar proportions of the acid and amine. The salts are usually water-soluble and can be conveniently recrystallized from various alcohols or from aqueous alcoholic solutions. They are relatively insoluble in acetone, ether, and aromatic hydrocarbons. They possess definite melting points, some of which are tabulated below.

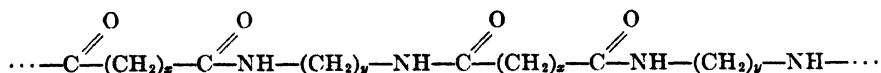
Table 30. Melting Points of Various Salts Prepared from Certain Diamines and Dibasic Acids⁸⁰

Diamine	Acid	Melting Point of Salt, °C
Tetramethylene	Azelaic	175–176
Pentamethylene	Sebacic	129–131
Hexamethylene	Adipic	183–184
Hexamethylene	Sebacic	170–172
Octamethylene	Adipic	153–154
Octamethylene	Sebacic	164–165
Nonamethylene	Adipic	125–127
Nonamethylene	Sebacic	159–160
Decamethylene	Adipic	142–143
Decamethylene	<i>p</i> -Phenylene diacetic	192–194
Undecamethylene	Sebacic	153–155
Dodecamethylene	Adipic	144–145
Dodecamethylene	Sebacic	157–158
- <i>p</i> Xylylene	Sebacic	210–212
- <i>p</i> Xylylene	<i>p</i> -Phenylene diacetic	250–252

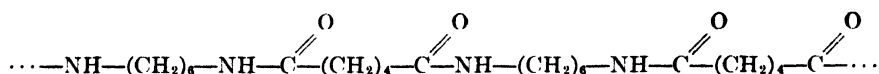
Control of salt formation can be established electrometrically, a fact which facilitates regulation of the relative quantities of reagents so that exactly equimolar amounts can be used. Values of the pH at the inflection point for solutions of typical nylon salts are 7.50 ± 0.10 for pentamethylene diammonium sebacate, 7.63 ± 0.3 for hexamethylene diammonium adipate, 7.71 ± 0.03 for decamethylene diammonium adipate, and 7.03 ± 0.10 for *p*-xylylene diammonium sebacate.

Upon heating these salts to temperatures within the range of 180 to

300°, depending upon the specific salt, time, and other conditions, they can be dehydrated quantitatively to polyamides possessing the general structure



This formula resembles that of the fiber forming natural proteins, but differs therefrom in that both acid groups are attached to one intermediate while both amino groups are attached to another. The most important nylon polymer at the present time is that derived from hexamethylene diamine and adipic acid. A portion of its structure may be indicated as follows:



Several types of nylon are now being produced, some of which represent different chemical compositions.

In order to prevent discoloration at the elevated temperatures used in preparing nylon by fusion of a salt, as well as during the spinning of a finished polyamide from a melt, reaction and subsequent extrusion should be conducted in an inert atmosphere, such as nitrogen or hydrogen. Salt dehydration and polymerization can usually be carried out without the use of catalysts, but various mineral oxides or carbonates and certain halides such as stannous chloride can sometimes be used advantageously. Antioxidants, especially those like syringic acid which do not discolor, may be incorporated in the reaction mixture.

Formation of polyamides from nylon salts need not necessarily be carried out by heating the dry salts. Any conditions favoring elimination of water may be employed. For instance, they can be heated in an inert solvent instead of being fused. Monohydric phenols—either phenol itself, cresols, xylenols, or other homologs or analogs of phenol—are the best and, indeed, almost the only solvents for the more refractory polyamides. Non-solvents like high-boiling mineral oils may also be used to facilitate heating, either alone or admixed with a phenol.

Preliminary preparation and purification of a nylon salt appears to be the most satisfactory means of proceeding in the production of a polyamide, because it affords a convenient way of ascertaining that the initial reactants will be present in chemical equivalency. It is, however, possible to use any other conventional means of forming an amide, such as direct reaction of dibasic acid and diamine at elevated temperature or reaction of a diamine with the anhydride, halide, or ester of a dibasic acid. Conditions required to form a polyamide vary according to the type of

amidation reaction. Thus, while temperatures of 180 to 300° and several hours of heating are employed in dehydrating and polymerizing a nylon salt by fusion, dibasic acid esters—especially phenolic esters—will form polyamides at temperatures as low as 50°. In the case of the reaction of dicresyl adipate with hexamethylene diamine, fiber-forming superpolymers can be obtained after heating for 2½ hours at 155°.

Polyamides are much less soluble in organic solvents than the corresponding polyesters and soften at higher temperatures. Like the polyesters, but unlike many other high polymers, they possess fairly definite melting points and soften within narrow temperature ranges. Approximate melting points, in air, of various fiber-forming superpolyamides are listed in Table 31.

Table 31. Approximate Melting Points of Some Fiber-Forming Polyamides^{8d}
(In the presence of air)*

Polyamide Derived from—	M.P., °C
Ethyl nediamine and sebacic acid	254
Tetramethylenediamine and adipic acid	278
Tetramethylenediamine and suberic acid	250
Tetramethylenediamine and azelaic acid	223
Tetramethylenediamine and sebacic acid	239
Tetramethylenediamine and undecanedioic acid	208
Pentamethylenediamine and malonic acid	191
Pentamethylenediamine and glutaric acid	198
Pentamethylenediamine and adipic acid	223
Pentamethylenediamine and pimelic acid	183
Pentamethylenediamine and suberic acid	202
Pentamethylenediamine and azelaic acid	178
Pentamethylenediamine and undecanedioic acid	173
Pentamethylenediamine and brassylic acid	176
Pentamethylenediamine and tetradecanedioic acid	170
Pentamethylenediamine and octadecanedioic acid	167
Hexamethylenediamine and adipic acid	250
Hexamethylenediamine and sebacic acid	209
Hexamethylenediamine and <i>beta</i> -methyl adipic acid	216
Hexamethylenediamine and 1,2-cyclohexanediactic acid	255
Octamethylenediamine and adipic acid	235
Octamethylenediamine and sebacic acid	197
Decamethylenediamine and carbonic acid	200
Decamethylenediamine and oxalic acid	229
Decamethylenediamine and sebacic acid	194
Decamethylenediamine and <i>para</i> -phenylene diacetic acid	242
<i>Para</i> -xylylenediamine and sebacic acid	268
3-Methylhexamethylenediamine and adipic acid	180
Piperazine and sebacic acid	153
Hexamethylenediamine and diphenic acid	157

* Melting points given in this table refer to observations made in the presence of air. In its absence, they may be quite different. For example, the melting point of the polyamide made from hexamethylenediamine and adipic acid is here given as about 250°, whereas in the absence of air it is about 263°.

In general, as the length of the unit chain increases and as the degree of substitution therein increases, the melting point diminishes and the solubility of the polymer in various solvents is augmented.

Much of the theory of nylon is an extension of the chemistry of linear polyesters discussed in the preceding chapter, to which reference should be made. As in the case of polyesters, low molecular weight cyclic diamides are readily produced where formation of a five- or six-membered ring system is possible. The most useful fiber-forming polyamides, therefore, are derived from dibasic acids and diamines in which the total number of carbon and nitrogen atoms in the linear skeleton of a monomeric structural unit is at least nine. It is, however, possible to prepare polyamides from diamines and dibasic acids capable of giving rise to a smaller structural unit, provided special care is observed. Fibers have been made, for instance, from polypentamethylene carbonamide, produced by reaction of dibutyl carbonate with pentamethylene diamine.

Like linear alkyds, polyamides are first obtained in the form of relatively low polymers possessing molecular weights of 1000 to 4000. These α -polymers cannot be spun into fibers, but they can be converted to spinnable ω -, or superpolymers, by continuing dehydration for a longer time or by altering the reaction conditions in such a manner that final traces of water will be removed and amidation will proceed substantially to completion. Reduced pressure may be used advantageously to assist the attainment of this state. It is, however, not essential to use vacuum; the reaction can be carried out under atmospheric or even increased pressure if provision is made for removal of water by some other means. The final stages of condensation in superpolyamidation can be hastened by agitation, by bubbling nitrogen through the reaction mass or above its surface. In such a case, however, traces of oxygen should be removed from commercial nitrogen before use in order to prevent discoloration of the polymer. Better results will ensue if the reactor is lined with silver, chromium, or chromium-containing ferrous alloys.

The viscosity of molten superpolymers is considerably greater than that of α -polymers, while the former dissolve more slowly than the latter in such solvents as phenol or formic acid, solution being preceded by swelling.

In general, a superpolymer must possess a molecular weight in excess of 7000 to exhibit fiber-forming properties. Staudinger has estimated that the molecular weight of commercial nylon is in the order of 12,500.

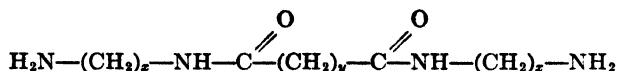
The viscosity of its solution in *m*-cresol affords a convenient means of control and permits the determination of the suitability of a polyamide for filament formation. If the intrinsic viscosity

$$\frac{\log_e \eta_r}{C}$$

is greater than 0.4, fibers can be drawn from it. Commercial fiber-forming products possess intrinsic viscosities of 0.5, to 2.0, usually 0.75 to 1.5. In the preceding formula, λ_r is the ratio of the viscosity of a dilute (0.5 per cent) solution of polymer in *m*-cresol to the viscosity of pure *m*-cresol at the same temperature, while *C* is the concentration of polymer in grams per 100 cc of solution.

If dehydration of a nylon salt is carried out in a phenolic solvent, decrease of conductivity is an indication of the extent of amide formation.

The ultimate extent of polymerization, and hence of viscosity, theoretically possible of attainment depends primarily upon the nature of the end groups present in a polyamide at any given instant. If one end group is carboxyl while the other is an amino radical, as would always be the case if a highly purified nylon salt were dehydrated or if a diamine were allowed to react with an exactly equimolar amount of a dibasic acid ester, for example, then reaction can continue indefinitely as long as dehydrating conditions are maintained and the ultimate molecular weight may be extremely high. Hence, the molecular weight of such a nylon would necessarily increase during spinning from a hot melt, resulting in rise of viscosity with the duration of spinning. This effect would be attended by alteration of physical properties and consequent lack of uniformity of spun filaments. In order to eliminate such troubles by preventing polymerization of molten polymer from proceeding beyond a given point, it is necessary to add a small excess of either one of the two reactants originally employed. In the presence of an excess of either, condensation will occur, theoretically, until all reactants are used up and the end groups become the same. With an extremely large excess of diamine, only a very low condensation product of one molecule of acid and two of diamine is formed:



With a very large excess of acid, a corresponding low molecular weight product is formed wherein carboxyls serve as both end groups.

As the excess of either reagent is decreased, however, the molecular weight of the polymer increases. Where the molar excess of either reagent is 5 per cent, or less, a polyamide is produced which can be spun. Usually at least 0.1 molar per cent excess of one of the reagents is essential in order to act as an effective viscosity stabilizer.

It is also possible to use either a monobasic acid or a monoacidic amine to stabilize the viscosity of a polyamide. In such a case the chain will be terminated by alkyl groups from the aliphatic acid or amine or, in the exceptional case of ammonia itself, by $-\text{NH}_2$ groups. The approximate

amount of a given stabilizer required to produce a nylon of a given intrinsic viscosity is subject to calculation.

The nature of the viscosity stabilizer affects the performance of nylon

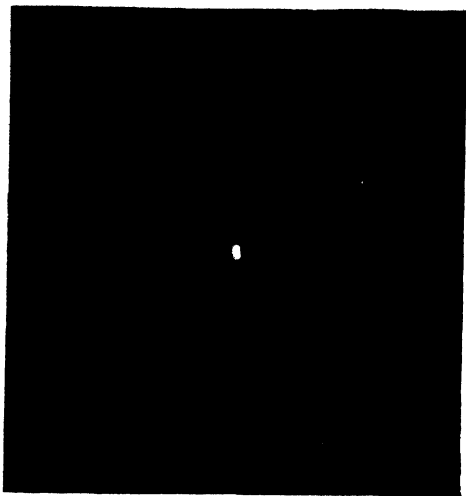


Figure 98. X-ray pattern of unoriented Type 66 nylon filaments.

Courtesy E. I. du Pont de Nemours & Co.

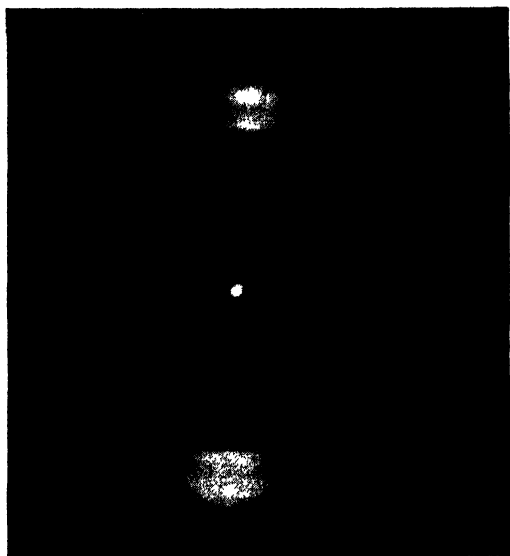


Figure 99. X-ray pattern of oriented Type 66 nylon filaments.

Courtesy E. I. du Pont de Nemours & Co.

on dyeing. Fibers prepared from dibasic acid-stabilized nylon are usually more readily dyed with basic dyes than are those made from diamine-stabilized polymers. Conversely, the latter possess greater affinity for acid dyes.

Like the corresponding polyesters, superpolyamides are microcrystalline. Fibers can be cold-stretched from two to seven times their original length, resulting in parallel orientation of the crystallites with attendant increase of elasticity, flexibility, toughness, and tensile strength, and with the development of strong birefringence and parallel extinction where observed under crossed Nicol prisms. Figures 98 and 99 show x-ray diffraction patterns of nylon 66 before and after cold stretching.

According to C. S. Fuller and coworkers at the Bell Telephone Laboratories, quenched nylon exists in a mesomorphous state for it does not give rise to such a clearly defined x-ray crystalline diffraction pattern as the same material cooled more slowly. Apparently the molecules are, so to speak, "frozen" in the state in which they exist in the liquid when the rate of cooling is very great. Upon slower cooling, however, a larger number of chains assume a more stable lattice-like arrangement. Annealing quenched nylon increases its crystallinity. Fuller and his collaborators have reported that a certain degree of mesomorphism is essential for cold drawing and have maintained that the properties of elongation, flexibility, and setting of stretched fibers can be accounted for by the presence of mesomorphous areas within oriented nylon. Well annealed, highly crystalline nylon can be cold-stretched only with difficulty, if at all.

Manufacture

Some ten kinds of nylon have been produced commercially, but not all of them represent different chemical compositions. Among chemical varieties, superpolyhexamethylene adipamide is currently the most important, for it is the material used in hosiery and other civilian applications of yarn as well as in all yarn for military needs. Both of its intermediates, hexamethylene diamine and adipic acid, may be derived from benzene through phenol. Adipic acid is made by oxidation of cyclohexanol, while hexamethylene diamine is manufactured catalytically from this acid, presumably by passing it over alumina in the presence of ammonia under high pressure.

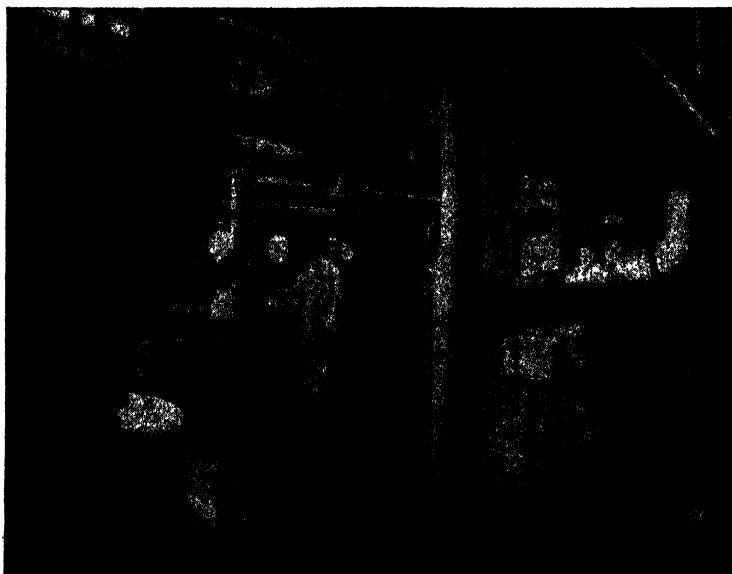
During World War II, adipic acid was manufactured in Germany from acetylene and formaldehyde by catalytic reaction in the presence of copper or silver acetylide. Butine-2-diol-1,4 thus formed was reduced to butanediol-1,4 which was then dehydrated to tetrahydrofuran. In the presence of nickel carbonyl as a catalyst this compound was then reacted with carbon monoxide to yield adipic acid. 5-Aminocaproic acid was also derived from acetylene and used in the production of polyamides.

The first step in the manufacture of nylon is formation of the corresponding salt by reaction of equivalent amounts of dibasic acid and diamine in aqueous solution. The exact point of neutralization is deter-



Courtesy E. I. du Pont de Nemours & Co.

Figure 100. First step in the manufacture of nylon yarn begins in this vessel, set in the floor of the du Pont plant at Seaford, Del.



Courtesy E. I. du Pont de Nemours & Co.

Figure 101. Autoclaves in the du Pont Company's nylon plant at Seaford, Del. In these receptacles polymerization takes place. Note the complex control panel, where every process is watched, and where lights and bells signal the operator as to the progress of each stage of polymerization.

mined electrometrically. Water is then evaporated from the salt solution and fusion of the salt is carried out at elevated temperature in an autoclave, with addition of a viscosity stabilizer. Amidation and simultaneous polymerization is carried out in an inert atmosphere. The viscosity stable polymer is then extruded in the molten state upon a huge casting wheel where it is immediately cooled by a water spray. At this point it is a translucent ribbon of tough, horny consistency somewhat resembling



Courtesy E. I. du Pont de Nemours & Co.

Figure 102. Molten nylon polymer, extruded on this huge casting wheel, is quickly sprayed with water which helps it to solidify into a strip resembling ivory. In later operations it is chopped, melted, and extruded again as filaments.

ivory. Upon removal from the wheel it is chopped into small pieces and subsequently passed into blenders where mixing is effected to ensure uniformity. The nylon chips are then ready for further processing.

Fabrication

The most important use of nylon is in the form of yarn. The chips are transferred to the hopper of a spinning unit where they drop onto a specially designed hot grid. Here the polyamide melts and is picked up by a pump which delivers it to the spinneret—a perforated flat disc—at a carefully regulated rate, after passage through a filter. The molten polymer is kept blanketed with an inert atmosphere, such as nitrogen, in order to prevent oxidation and consequent discoloration.



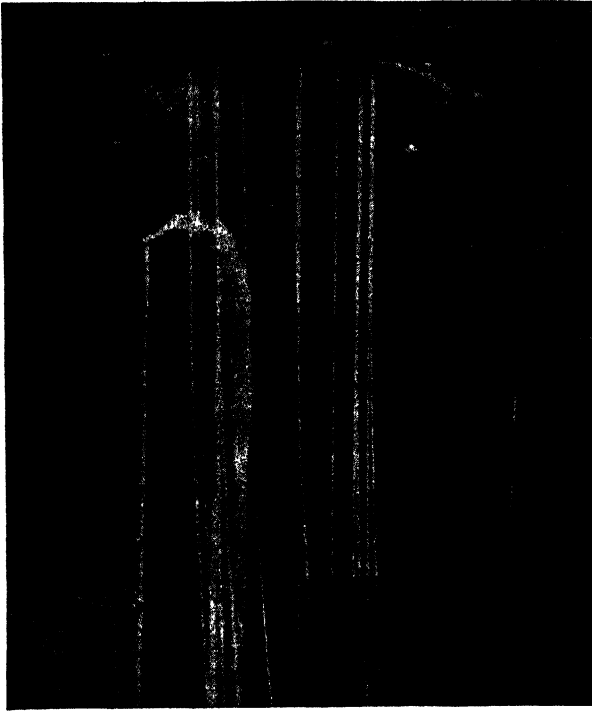
Courtesy E. I. du Pont de Nemours & Co.

Figure 103. Nylon flake pours from the hoppers. These flakes, or chips, are made by chopping the long, ivory-appearing strips that are extruded after polymerization has been completed. The flakes are melted and the molten material is again extruded in filament form. Nylon flake is also shipped for use in the manufacture of brush stock, electrical insulation, etc.



Figure 104. Nylon, as delivered to the du Pont Plastics Department in the form of flakes, is fed into the hopper of a spinning machine where it is melted and extruded into filaments.

Courtesy E. I. du Pont de Nemours & Co.



Courtesy E. I. du Pont de Nemours & Co.

Figure 105. The birth of nylon filaments. From tiny holes in this spinneret are extruded these fine filaments of nylon. All of the filaments shown here will be wound together to form nylon yarn.



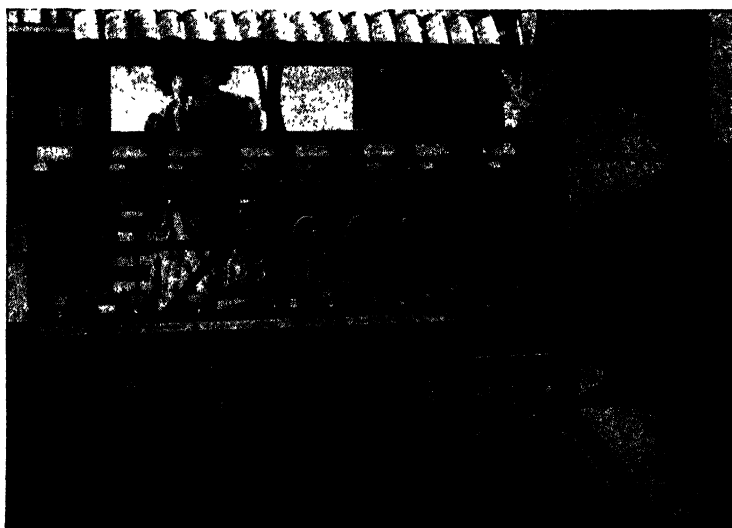
Courtesy E. I. du Pont de Nemours & Co.

Figure 106. Batteries of machines like these wind nylon yarn onto spools after the filaments have been extruded from the spinnerets. From here the nylon goes into the textile area and is given treatments similar to those of other fine yarns.



Courtesy E. I. du Pont de Nemours & Co.

Figure 107. Sizing nylon yarn. The yarn is wound from one spool to another, passing over a gummy substance which gives it added protection during textile manufacturing operations. It is subsequently removed from the finished products.



Courtesy E. I. du Pont de Nemours & Co.

Figure 108. Nylon filament to be used as sutures or fishing leaders is shown in this photograph being wound upon spools preparatory to shipment.

Heating grids, pumps, and spinnerets were all designed specially for handling nylon because high temperature extrusion of a molten polymer was a new departure in the textile field. The pump represented a particularly serious problem, for it has to deliver a precisely regulated amount of polyamide accurately to the spinneret. The only permissible lubricant is molten nylon itself. Special non-warping, abrasion-resistant steels are required which are capable of withstanding constant exposure to the spinning temperature of 285°.

Molten nylon is forced through the holes of the spinneret by the pressure of the pump. Upon emerging into the cooler outside air, it rapidly hardens and is wound up on bobbins at nearly thirty miles an hour (2500 feet per minute). The diameter of the extruded filaments is determined largely by the rate at which molten polymer is supplied to and drawn away from the holes of the spinneret.

Cold-stretching takes place immediately after spinning. The individual filaments are gathered and coated with a film of light lubricant and wound up on bobbins from which they are at once transferred to other bobbins of the same size, running four times as fast. The yarn is thereby stretched to four times its original length, "necking" down to half its former diameter. It is then twisted, wound on cones, spools, or bobbins, and baked in ovens to set the twist.

Natural silk is coated with sericin which protects the fiber and facilitates handling in textile operations. It is later removed. Approximately 20 per cent of the weight of raw silk is lost by this degumming process. Nylon, of course, contains no sericin and, in some applications, has to be coated with a specially developed size before it can be woven or knitted. The size is subsequently eliminated. Sizing may be carried out either before or after the yarn is shipped to the fabricator. Compositions comprising polyvinyl alcohol have been found especially advantageous in application from aqueous solution. Various proprietary compositions, such as "Pro-Nyl," have lately been developed for sizing from organic solvents.

Nylon can be delustered by incorporation of titanium dioxide in the melt before spinning. It can also be colored by addition of suitable dyes or pigments to the melt, although it is more customary to dye the finished goods by conventional methods. Currently, acetate dyes are preferred. Many other types of dyestuffs can be used, however, if desired, especially acid, wool, and mordant colors.

By somewhat similar processes, nylon can also be extruded into relatively coarse monofilaments for use as a bristling filament and other applications. Monofilaments are available in diameters ranging from 0.005 to 0.002 inch. By progressively varying take-off speeds during extrusion, tapered bristles are produced for use in paint brushes.

Nylon has also been extruded on a developmental basis in the form of rods and tubing several eighths of an inch in diameter.

Injection-molded articles of nylon have appeared recently. They have been used in limited quantities in military applications. Because of the high melting point of the type of nylon utilized for this purpose, unusually high molding temperatures are required—in the order of 530° F. Inasmuch as this point is close to the decomposition temperature of the material, exceptional operating care must be observed. Because of its sharp melting point, nylon is much more fluid at molding temperatures than most other thermoplastics in common use. A shutoff mechanism therefore must be employed in the nozzle of the injection molding machine in order to prevent excessive oozing out of molten plastic. For the same reason, special precautions must be taken to preclude the formation of excessive flash in the mold. The latter should be designed with large cold-slug wells not only at the end of the sprue, but also at the ends of all major runners.

Nylon is used in solution form in wire and fabric coating and in various other surface finishes. While polyhexamethylene adipamide is appreciably soluble only in formic acid and in phenolic bodies, certain other types of nylon possess greater solubilities. Nylon type 6, for example, can be dissolved in 80 per cent isopropyl alcohol.

Nylon film is likewise under experimental development, while foamed nylon and numerous other fabricated forms are mentioned in the patent literature.

Properties

The crystalline character of nylon has already been discussed. Orientation of the crystallites by cold-drawing greatly increases tensile strength. The tenacity of various nylon yarn types as currently made ranges from 5 to 8 grams per denier. A tensile strength of 7.5 grams per denier, typical of the yarn offered for tire cord and tow rope, corresponds to approximately 109,000 lbs/sq in. (Raw silk has a tensile strength of about 64,000 lbs/sq in; degummed silk, about 45,000 lbs/sq in.) Knot tenacity, depending upon the type of knot, may vary between 70 and 97 per cent of its normal strength.

Stress-strain curves for nylon, silk, viscose, and acetate silk are shown in Figure 109.

The cold-drawing of nylon also markedly decreases brittleness. Its impact strength has been reported as 1.5×10^{-3} inch pounds per denier per inch length.

One of the most remarkable results of cold-stretching is the development of elasticity after the fiber has reached the maximum length permitted by cold-drawing. This property is of especial importance in

hosiery and in tow ropes for gliders. It will be seen from Figure 109 that, at loadings below about 0.5 gram per denier, nylon is much more extensible than the other fibers mentioned. The extensibility and elastic recovery of nylon yarn is compared with that of Italian silk and viscose in Figures

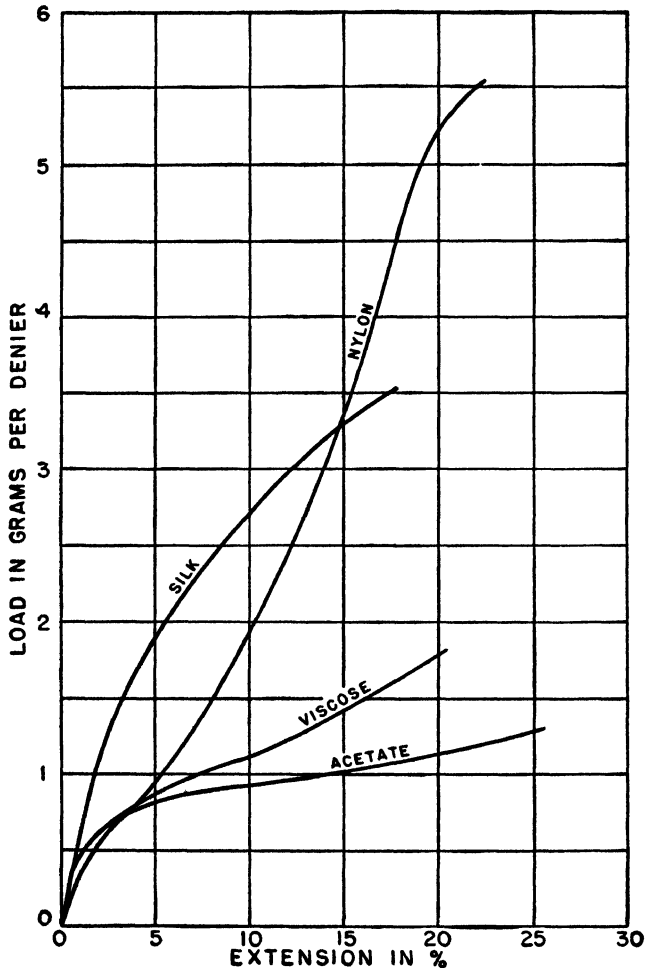


Figure 109. Stress-strain curves for nylon compared with other textiles. (Loasby²⁰)

110–112. The data plotted in these figures were obtained by use of a Scott Inclined Plane Tester, increasing the load at the rate of 4 grams/denier/minute and reducing it at the same speed, a one-half minute interval being allowed after the completion of each hysteresis loop before beginning the next one.

Polyamides are only slightly affected by moisture. Figure 113 gives a comparison of the wet and dry strength of various textiles. Nylon yarn absorbs less water than most other textiles, as shown in Figure 114, and therefore dries rapidly after washing.

An important characteristic of nylon is its ability to shrink slightly

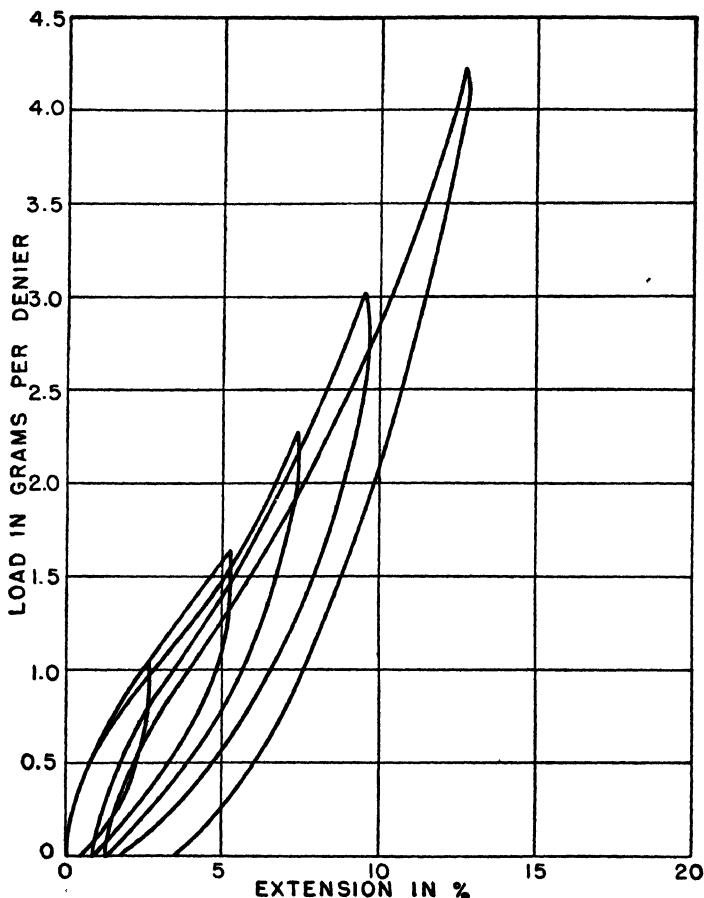


Figure 110. Stress-strain hysteresis loops for nylon. (One-half minute recovery with no load.) (*Loasby*²⁰)

and take a permanent set upon exposure to an elevated temperature, as by steaming. Advantage is taken of this fact in the pre-boarding of hosiery after knitting, but before dyeing, whereby it is given the desired permanent shape. Reheating to temperatures above that of the initial set permits reshaping of the goods. The set given to hosiery is imparted at temperatures considerably higher than those encountered in laundering.

Proper treatment of nylon in this manner also minimizes subsequent creasing and wrinkling.

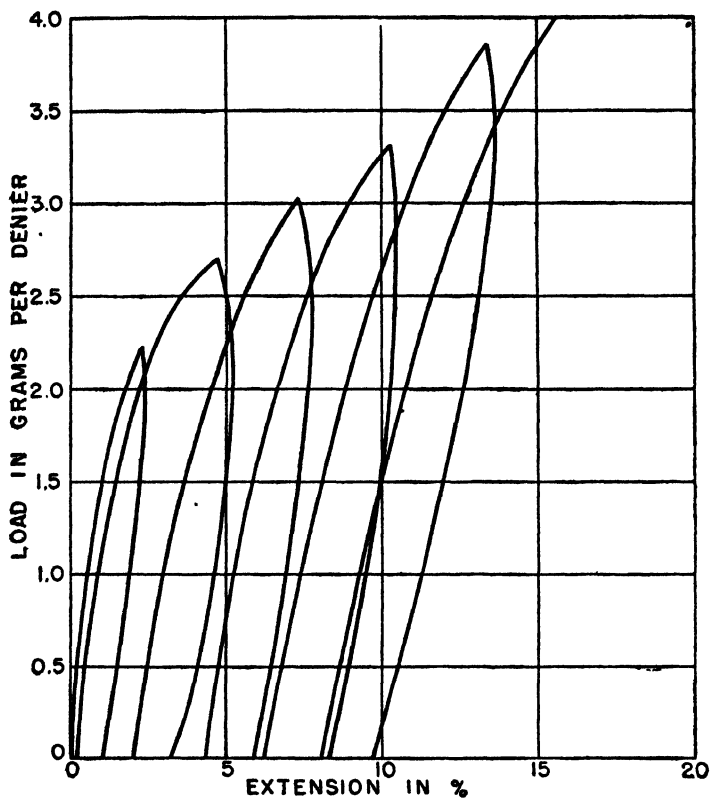


Figure 111. Stress-strain hysteresis loops for Italian silk. (One-half minute recovery with no load.) (*Loasby*²⁰)

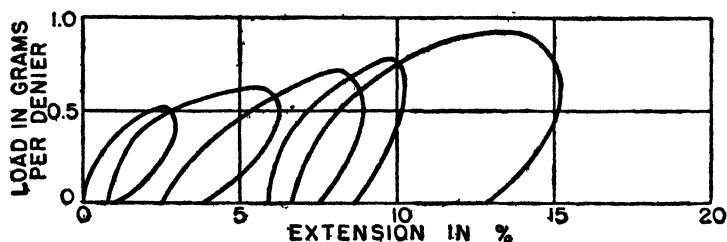
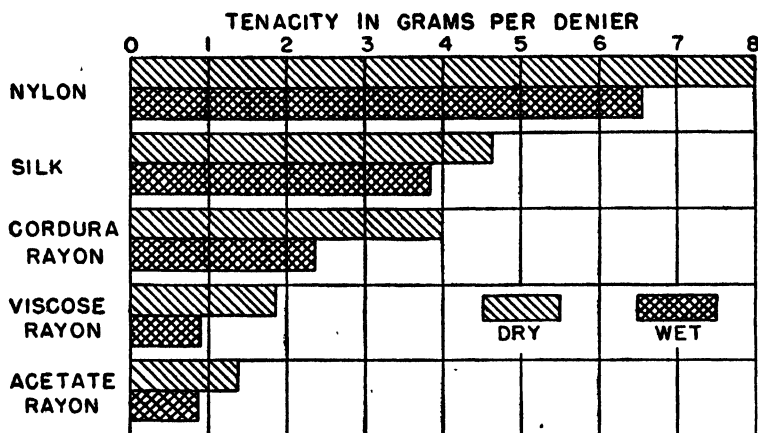


Figure 112. Stress-strain hysteresis loops for viscose rayon. (One-half minute recovery with no load.) (*Loasby*²⁰)

The resistance of polyamides to heat and solvents has already been noted. These characteristics are especially pronounced in hosiery-type

nylon. They can be varied to some extent by altering the chemical nature of the intermediates, as illustrated previously in Table 31. Polyamides are relatively nonflammable and are not attacked by mildew, mold or other fungi.



Courtesy E. I. du Pont de Nemours & Co.

Figure 113. Wet and dry strength of nylon compared with other fibers.

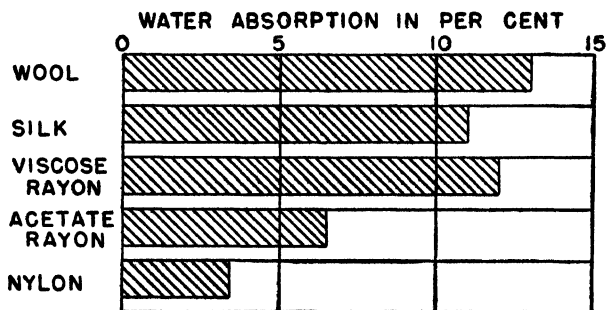


Figure 114. Water absorption of nylon compared with other fibers (60 per cent relative humidity).
(Adapted from Hoff¹⁷)

Nylon, like other textile materials, deteriorates somewhat upon exposure to ultraviolet light, but its performance in this respect is superior to that of silk.

Table 32 lists various properties of nylon yarns now being made, while the characteristics of bristle material are shown in Table 33. Properties of one type of molded nylon, FM-1, are given in Table 34.

Table 32. Physical Properties of Nylon*

(Type now used for yarn)

A. Mechanical Properties of Drawn Fibers:

1. Tensile strength, dry: about 5 to 8 grams per denier.
2. Tensile strength, wet: about 80 to 90 % of dry strength.
3. Elongation, dry: about 20 %, but can be varied widely, depending on degree to which yarn has been drawn.
4. Elongation, wet: about 25 %, can be varied widely.
5. Loop strength, dry: 90 % of tensile strength.
6. Elastic recovery, against no load:

% Stretch	% Elastic Recovery
2	100
4	100
8	100
16	91

(Fiber held under tension for 100 sec;
60 sec allowed for recovery.)

7. Modulus of elasticity (resistance to stretch):

To stretch boiled-off yarn 1 % requires a minimum of 0.3 g per denier. Calculated modulus of elasticity; 300 kilograms per sq mm or 4.6×10^5 pounds per sq in. Stress-strain curve approximately linear up to 4 % stretch.

B. Density:

The density of dry nylon fibers is about 1.14.

C. Thermal Properties:

1. Heat capacity (average) between 20° and 265° C: 0.555 cal/g/° C.
2. Heat of fusion: 22 cal/g.
3. Heat resistance:

100° C, steam, 6 days: very slight effect on tenacity.

65° C, air, 4 months: about 5 % loss in tenacity.

200° C, no oxygen, 3 hours: no change in tenacity.

4. Ironing: no effect on tensile strength for iron temperatures up to 180° C. At 135° C creases are removed. Above 180° C, sticking may occur; above 230° C damage starts.

5. Setting: hot water or saturated steam will set fiber in shape it is held in, *e.g.*, straight or creased, and such setting is only partially reversible. Effect roughly proportional to temperature and to logarithm of time (meaning that a moderate increase in temperature is more effective than a moderate increase in time).

D. Hygroscopic Properties:

1. Moisture content 4.5 % at 75° F–72 % relative humidity.
2. Linear change: the wet length of nylon fibers is about 2.5 % greater than the bone-dry length.

E. Optical Properties:

1. Refractive index: 1.53 to 1.57; highly double refracting.
2. Absorption (measurements were made on nylon film 0.002 cm thick, equivalent to the diameter of a 2.5 denier filament):

Wave Length Angström Units	% Absorption
2350	80
2550	10
3300	6
3400	5
3600	0

F. Electrical Properties:

1. Volume resistivity: 4×10^{14} ohm-cm at 18% R. H.
 5×10^9 ohm-cm when wet.
2. Dielectric constant: 4 at 1000 cycles, at 18% R. H., 22° C.
3. Power factor: 5% at 1000 cycles, at 18% R. H., 22° C.
4. Breakdown strength: 1300 volts/mil for 9 mil thickness, sheet not rolled.
3000 volts/mil for 2 mil thickness, sheet rolled.

G. Chemical Resistance:

1. Bleaching agents: Bleaching agents such as sodium peroxide, sodium hypochlorite, sodium chlorite, sodium perborate and hydrogen peroxide do not bleach nylon. If used in normal bleaching concentrations at temperatures much above 110° F these agents will seriously degrade the yarn.
2. Acids: Hot mineral acids will hydrolyze nylon, particularly if they are concentrated.
3. Alkalies: Sodium hydroxide of 10% concentration at 85° C for 16 hours causes no apparent degradation of nylon.
Potassium carbonate in 19% concentration at room temperature for 2 months causes a loss of 3% in strength.
4. Various solvents: After 2½ to 3 days' immersion in the following solvents no strength loss of the nylon was apparent: methanol, benzene, carbon tetrachloride, acetone, solvent naphtha and benzene-ethanol 50 : 50. No data are available on the effect of these solvents on the dyes on nylon.
5. "Freon" fluorinated refrigerants: Liquid "Freon 12" (dichloro-difluoro-methane) at room temperature for 8 days does not decrease tenacity.
6. Nylon polymer is substantially inert to virtually all organic acids except formic acid and the phenols (which are solvents); to halogenated hydrocarbons, alkalies, soaps, and to aldehydes, ketones, and alcohols in general.

H. Solubility:

1. Nylon is readily soluble at 25° C in the following solvents: Phenol, *m*-cresol, xyleneol, formic acid.
2. Solvents dissolving 1% at 25° C: Crotyl phenol, secondary amyl phenol, *o*-allyl phenol, glycerol monochlorhydrin, glycerol dichlorhydrin, ethylene bromhydrin, ethylene chlorhydrin, acetic acid, lactic acid, thioglycolic acid, 2,3-dibromopropanol, phenyl ethyl alcohol.
3. In addition to the above, a few other compounds are solvents for nylon at elevated temperatures.

I. Flammability:

Pure nylon is virtually nonflammable. When brought into contact with a flame, fabric made from nylon yarn in its pure state simply melts. Although the molten nylon is ultimately consumed if kept in the hot flame, the fabric itself does not blaze or propagate flames. Nylon fabrics can be made to burn if impregnated with certain dyes, oil finishes, or catalyzing chemicals.

J. Heat Yellowing:

After treating for 5 hours at 150° C in air the relative yellowing of a series of fabrics was as follows:

Silk — brown
Wool — yellow
Nylon — light yellow
Viscose and acetate rayon — still lighter yellow
Cotton — barely noticeably darkened.

* Manufacturers' data, E. I. du Pont de Nemours & Co., Inc. (Cf.¹⁰)

Table 33. General Physical and Chemical Properties of Nylon for Industrial Brushes *

Melting Point (in absence of oxygen) — ° C	263
(10–15 degrees lower in presence of oxygen)	
Density	1.15
Modulus of Elasticity — psi	
At 0% relative humidity	0.70×10^6
At 50% relative humidity	0.45×10^6
At 100% relative humidity	0.17×10^6
Tensile Strength — psi	50,000
Elongation to Break — %	20–30
Abrasion Resistance: Far superior to hog bristle, tough rather than brittle.	
Moisture Absorption: $\frac{1}{2}$ that of hog bristle.	
Solubility: Soluble in cresol, phenol, formic acid and concentrated mineral acids.	
Exposure: Bristle properties unaffected by exposure conditions ranging from — 14° to 65° and relative humidities ranging from 0 to 100%.	
Oxidation: Yellows slightly on long exposure at temperatures above 100° in presence of oxygen.	
Chemical Resistance:	

Chemical Agent	Time of Exposure	Effect on Bristle Properties
Satd. sodium perborate soln.	24 hrs	None
Satd. sodium perborate soln.	14 days	Slight decrease in tensile strength and stiffness, abrasion resistance unaffected.
Hydrogen peroxide	24 hrs	None
Trisodium phosphate, 10% soln.	3 wks	None
Soda ash, 10% soln.	3 wks	None
Trisodium phosphate and soda ash (1 : 1), 20% soln.	3 wks	None
Sodium cyanide, 10.4% soln.	7 days	None
Potassium carbonate, 19% soln.	2 mos	None
Acetic acid, 5% soln.	2 mos	None
Sulfuric acid, 5% soln.	7 days	None
Hydrochloric acid, 5% soln. at 100°		Slowly decomposes
Sodium hydroxide, 1% soln.	2 mos	None
Sodium hydroxide, 10% soln. at 85°	16 hrs	None
Lard at 82°	5 days	None
Cottonseed oil at 82°	5 days	None

Applications

Nylon finds its principal use as yarn, in which form it has been universally acclaimed not as a mere substitute for silk, but as a superior product in all of its many applications. Many consumer goods knitted or braided of this textile, woven, or stranded, have made their appearance. Full-fashioned and seamless hosiery, half-hose and anklets, corsets, girdles, underwear, nightgowns, negligees, hostess gowns, and gloves are typical of the many varieties of women's wearing apparel made in whole or in part of nylon. Marquisettes, mousselines, and other sheer dress goods have appeared. Men's hose and ties have also been introduced. Wrinkle-free shirts may be a future development. Water-proofed nylon has been

Table 34. Typical Properties of FM-1 Nylon¹ (For Injection Molding)

Property	Test Method	Test Result
Specific gravity	D71-27	1.14
Tensile strength - 70, 77, 170° F, psi	D638-42T	16,620 ^a ; 10,530; 9,290 ^b
Elongation - 70, 77, 170° F, %	D638-42T	3 ^a ; 54; 145 ^b
Modulus of elasticity, 77° F, psi	D638-42T	325,500
Flexural strength, 77° F, psi	D650-42T	12,600-14,600
Impact strength, Izod - 70, 77, 170° F, ft lb/in	D256-41T ^a	0.418; 0.944; 0.968
Stiffness, 77° F	Arlington M-9	1.89-2.02 ^c
Rockwell number	Arlington M-29	100 L; 65 H
Creep in flexure	Arlington P-25	89 ^d
Deformation under load, 122° F, %	D621-41T	4.0
Heat distortion temperature, ° F	D648-41T	149
Heat distortion temperature, low load, ° F	D648-41T	403 ^e
Specific heat, cal./gm/° C	—	0.55
Coefficient of expansion per ° F	D696-42T	5.7 × 10 ⁻⁵
Thermal conductivity, B.t.u./hr/ft ² /° F/in	D825-31T	1.74
Dielectric strength, short time, V/M	D149-39T	400
Dielectric strength, step by step, V/M	D149-39T	300
Volume resistivity, ohm-cm	D257-38	10 ¹³
Dielectric constant, 60, 10 ⁴ , cycles	D150-41T	3.8 ^f ; 4 ^g
Power factor, 60, 10 ⁴ , cycles	D150-41T	1.8 ^f ; 5 ^g
Water absorption, %	D570-42	1.5
Flammability, in./min	D635-41T	Self extinguishing
Methods of working		Injection, extrusion
Basic color		Light cream
Resistant to		Esters, ketones, alkalis, alcohols, common solvents, weak acids.
Not resistant to		Phenol, formic acid, concentrated mineral acids.
Outstanding for		Toughness, high temperature resistance, ability to injection mold into thin sections
Major uses		Heat-resistant parts

^a - 53° F; ^b 140° F; ^c Millimeters deflection at 0.125 in thickness; ^d Mils after 48 hr at 1600 psi and 77° F - original deflection; ^e 64 psi - D648-41T mod.; ^f 33° C dry; ^g 22° C, 18% RH, 10⁴ cycles; ^h Type R conditioning.

used in shower curtains, umbrellas, raincoats, light tenting, and numerous other items.

Of major importance in military applications have been parachute cloth and shroud lines for the air services. Nylon parachutes have been successfully tested with dummies by opening them immediately after release from planes flying at speeds of 400 miles per hour. The resistance of nylon to salt water and mildew are other characteristics which have favored its use in this application, for silk parachutes must be carefully washed and dried immediately after falling into the sea if they are to be used over again. Mildew resistance is also a major reason for military use of nylon yarn in nettings and screenings, jungle hammocks, ponchos, shoe laces, and electrical insulation in the tropics.

Other textile uses of nylon are in staple fiber, as differentiated from continuous single and multifilament yarns. Staple fiber, resembling wool in appearance, has been spun into yarns for darning thread, sweaters, swim suits, sport hose, and ladies' coats. Mixtures of nylon staple fiber with other fibers offer interesting possibilities.

Numerous tapes, webbings, and plied and braided nylon products have acquired industrial and military importance. They include fish lines, sewing thread, typewriter ribbons, surgical sutures, watch straps and bracelets, shoe laces for military use, webbings for parachute harness, bomb slings, gunners' belts, and tow ropes for gliders. Nylon has been especially useful for the last application inasmuch as rope made therefrom stretches up to 40 per cent of its length and thus, in combination with a special mechanical device, helps to absorb the initial pick-up shock without discomfort to the occupants of the glider. This military use was an outgrowth of the earlier development of nylon rope for airmail pick-up duty.

Nylon cord has found wide acceptance for severe service in military tires. Its great strength and lightness have enabled the largest bombers and cargo planes to carry ever-increasing loads without enlarging the size and weight of the tires. The fastest fighters and largest planes landing at high speeds on small, front-line, improvised fields—many of which were laid on jagged coral formations—have tested to the maximum the bruise and shock resistance of nylon cord. Landing at high speed on small fields when brakes had to be jammed on hard in order not to overrun the landing area caused the tread of tires to buckle and fold back on itself at the moment of contact. Nylon has given satisfactory performance under such trying conditions in actual military service.

Nylon monofilaments of various sizes have been used in super-sheer hose, in corrosion resistant screening which has seen tropical military service, and in manifold bristle applications. The brush industry has, in

fact, been revolutionized by the introduction of nylon bristles. First appearing in 1938, under the trade-mark "Exton," in Dr. West's "Miracle Tuft" toothbrushes, nylon bristles surged forward into use in more than four-fifths of all high quality toothbrushes and in more than half of all domestic hairbrushes by the end of 1941. Clothesbrushes, nail-, complexion-, and household cleaning brushes represent consumer goods that have been bristled with nylon to advantage. Industrial brushes in great profusion have also made use of nylon bristles, including those employed in bottle-labelling, pipe-cleaning, fabric printing, bottle-washing, vat scrubbing, dry cleaning and textile fabrication, metal plating, sewage disposal, and vacuum cleaner construction. Cannon swabs have been equipped with nylon bristles. Tapered bristles for paint brushes have already been mentioned.

Other uses of nylon monofilaments include tennis and badminton racquet strings, surgical sutures, fishing leaders and snells, nylon-wound instrument strings, and miscellaneous special shapes such as rattan for outdoor furniture and public conveyance seats.

Nylon, either melt-extruded or in solution form, is being used to insulate electric wire for many purposes where high abrasion resistance, coupled with a minimum addition to the bare wire diameter, is necessary.

Molded nylon bearings have given excellent service, especially in textile machinery. They are said to be satisfactory where lubricated with water or under light loads without any lubrication. Coil forms of nylon have been used by the Navy in sound-powered telephone units. Various other military moldings have been made of nylon. Molded nylon zippers appear to be a possibility.

Other developmental applications of nylon include such diverse items as neoprene-impregnated carburetor diaphragm fabric, machinery packing, and transparent film.

The price of nylon naturally varies, depending upon the form in which it is produced. It is expected, however, that it will be competitive, price-wise, in the various fields where it will be used. For example, it is anticipated that tapered nylon bristles for paint brushes will, at most, cost not more than high-quality pig bristles of the same length, and probably will be considerably lower in price. It is anticipated also that price reductions for all forms of nylon will go hand in hand with improved methods of manufacture and increased production.

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Chapter 13

Coumarone-Indene Resins. Miscellaneous Hydrocarbon Resins

Coal distillates are a fruitful source of cyclic unsaturates containing the double bond in non-benzenoid rings. Two coal tar compounds of this type, coumarone and indene, have been converted to useful commercial resins for some thirty years. Despite these facts, however, surprisingly little systematic scientific and technical study has been devoted to the polymerization of cyclic olefins and diolefins. Insufficient evidence has, therefore, been obtained to permit the formulation of general rules concerning their polymerization. Under special conditions a few of them, notably cyclopentadiene, have been polymerized to high degrees. Polymers obtained under customary conditions, however, including all commercial representatives of this class, are hemicolloidal in character.

There are at present three general categories of cyclic unsaturates which are converted to industrial resins. The oldest and most important of this group are the two analogs just mentioned, coumarone and indene. A second class of such monomeric materials is to be found in non-coal-tar products—the terpenes. Finally, cyclopentadiene has recently become the source of certain commercial and semi-commercial polymers.

Cracked petroleum distillates also contain a goodly portion of unsaturated hydrocarbons. The chemical nature of these materials is less clearly understood than in the case of their coal tar analogs, but they probably comprise both open and closed chain mono- and diolefins. Certain polymeric compounds are obtained from this source.

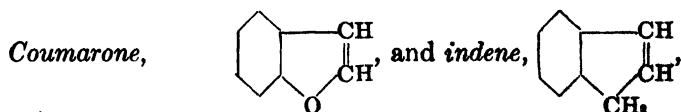
A number of miscellaneous resins have also been derived from aromatic hydrocarbons in recent years by various condensation reactions.

Coumarone-Indene Resins

The earliest detailed experiments with resins from coumarone and indene appear to have been carried out by the German chemists, Kraemer and Spilker, in 1890. During World War I shortages of natural resins in the Central Powers led to development of these resins there on a moderately large scale. Industrial evolution of these plastics in the United States began soon afterwards, but was at first hampered by difficulties in

control of quality. In the field of one of their principal outlets, varnishes, they were one of the first purely synthetic resins to make their debut in a serious way. Their general acceptance was therefore slow, for the industry was not yet acclimated to the introduction of synthetic resins as bases for modern finishes.

Several of the earliest American patents relating to coumarone-indene resins were granted to Marc Darrin and his collaborators. Production was first undertaken by the Barrett Company in 1919. Then, at about ten year intervals, two other concerns entered the field: The Neville Company and the Pennsylvania Industrial Chemical Corporation.



both occur in the solvent naphtha cuts of coal tar distillates. They are colorless liquids which boil at 172 and 182°, respectively. The average content of these chemicals in dry coal tar is about 0.6 per cent, with indene preponderating. Because of the proximity of their boiling points, they are difficult to separate. Indeed, no effort is usually made to remove either of them from the naphtha in which they occur. On the contrary, resinification is used as a means of separating them from other more saturated components of this cut which are subsequently distilled and sold as solvents.

In commercial operations, sulfuric acid is employed as the resinifying agent, although numerous other catalysts are also effective and have been used in the laboratory or for the preparation of special high-melting resins.

In order to control quality and obtain useful products which are not black, sticky gums, it is necessary to observe careful fractionation of the solvent naphtha used. Sometimes, for the highest quality grades, a preliminary wash of the distilled naphtha with a small amount of sulfuric acid is desirable to remove highly unsaturated hydrocarbons which yield dark colored products upon resinification. A fraction of one per cent of concentrated sulfuric acid may be used in this treatment, or as much as 4 to 5 per cent of 66 per cent acid. After separation of the sludge, still further purification is sometimes carried out for the best products. The final resinification operation is then conducted by treating the product with sufficient sulfuric acid to cause polymerization of its coumarone-indene content.

Factors determining the character of the finished resin are primarily:

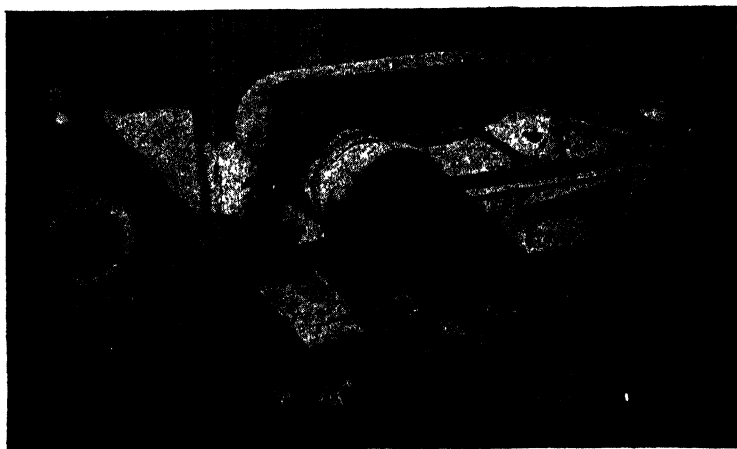
- (1) Degree of purification of naphtha from tar-forming components.

Obviously, for the best-colored grades of resin, tar-forming impurities must be reduced to a minimum. Particularly obnoxious in this respect are



Figure 115. Vacuum steam still used in manufacturing coumarone-indene resins.

Courtesy The Neville Co.



Courtesy The Neville Co.

Figure 116. Flaking coumarone-indene resin.

styrene, cyclopentadiene, and dicyclopentadiene. To eliminate tar-forming impurities as much as possible, modern practice tends towards the use of 160–190° cuts for naphthas employed in making the best grades of coumarone-indene resins.

(2) Concentration of coumarone-indene in the solution. The amount of these unsaturates in the purified naphtha usually runs between 30 and 85 per cent. When the concentration exceeds the former figure, control of temperature during resinification is difficult and recourse is had to dilution with an inert solvent such as petroleum naphtha.

Although probably not a particularly important factor in commercial operations, it appears that the molecular weight of the polymer decreases somewhat with dilution of the monomer by inert solvent. The relation between concentration of monomeric indene in benzene solution and its degree of polymerization at 5°, upon treatment with a given amount (approximately 5 per cent) of stannic chloride as catalyst, has been found by Staudinger and his co-workers to be as shown in Table 35.

Table 35. Relation between Concentration of Indene in Benzene Solution and Its Degree of Polymerization in the Presence of Stannic Chloride at 5°¹⁷

Concentration of Indene in Benzene Solution (per cent)	Yield of Polyindene (per cent)	Properties of Polyindene	
		Molecular Weight.	Softening Point (° C)
50	100	3670-3850	220
10	80	3240-3470	205
1	50	2350-2300	195

(3) Temperature of polymerization and temperature control during reaction. By using equal amounts of stannic chloride catalyst in 8 per cent toluene solutions of indene, Staudinger and his collaborators also found that the degree of polymerization of the resin formed decreased as the temperature increased from - 80° to + 50°. At higher temperatures their results were inconclusive.

Table 36. Relation Between Temperature and Molecular Weight of Polyindene Formed in the Presence of Stannic Chloride¹⁷

Temperature of Polymerization (° C)	Molecular Weight of Polymer
- 80	3500
- 20	3300
+ 50	1200

In commercial practice, the temperature of resinification is usually held at 20° or lower. For the highest melting and lightest colored products, sub-zero temperatures are used.

(4) Concentration and amount of sulfuric acid used. Acid of 93 per cent concentration or stronger is usually employed. The amount varies with other reaction conditions, usually running between 500 and 1000 pounds per thousand gallons of naphtha.

(5) Rate of addition of sulfuric acid and time of reaction. These factors must be adjusted in such a manner as to maintain a low temperature throughout reaction.

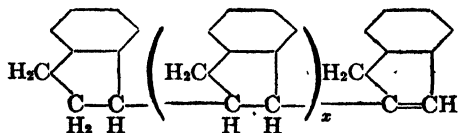
(6) Degree of admixture of catalyst and naphtha. Thorough agitation by means of efficient and vigorous stirrers is essential.

(7) Conditions of removal of solvent from resin. After resinification, separation of sludge acid from the supernatant resin solution is effected as quickly as possible by settling and withdrawal of the bottom layer. The resin solution is then washed with caustic and water and the unreacted naphtha, together with added solvent, is distilled off in a steam-jacketed vacuum still, leaving behind the coumarone-indene resins as a residue. Distillation is continued until softening point determinations run upon sampled portions of the residue attain the temperature desired. To prevent discoloration of the resin and to yield the highest-melting products, the temperature of distillation should be kept as low as possible. Temperatures below 275° are essential, inasmuch as decomposition of these resins begins to occur at that point. Best results are said to be obtained below 90° by application of vacuum where necessary.

The distillate is separated into naphthalene, various solvent naphtha cuts, and high-boiling oils sold as special solvents and plasticizers.

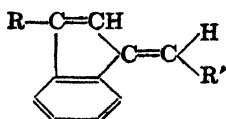
The molecular weight of the highest melting commercial coumarone-indene resins is in the order of 800 with a degree of polymerization of about 6 to 7. Lower melting resins possess a lesser degree of polymerization.

The structure commonly assigned to these products, exemplified by that of polyindene, is as follows:



Because of the presence of a double bond in the end group of their relatively low molecular weight structure, these resins possess an appreciable amount of unsaturation. Their iodine numbers run from 15 to 60, where account is taken of substitution during determination.

As a result of the cyclopentadiene structure present in the end group of these resins, they are capable of undergoing fulvenation, *i.e.*, reaction with an aldehyde at the reactive methylene group, to give a cross-conjugated structure as follows:



Cross-conjugate systems are chromophoric groups. Upon long exposure of films of coumarone-indene resins to the atmosphere, discoloration de-

velops. It has been hypothesized that this phenomenon can be attributed to fulvenation as a result of preliminary aldehyde formation by oxidation of the double bond of some of the molecules present. Because of this tendency towards discoloration, coumarone-indene resins are not employed in surface coatings where extremely good color retention is essential. Hydrogenation eliminates the double bond and improves color and color stability.

Coumarone-indene resins, sometimes called paracoumarone-indene, are produced in a wide variety of melting point ranges varying from viscous liquids at room temperature to friable solids, often flakes, melting at 150 to 160°. The solid varieties are all brittle, somewhat resembling rosin in physical appearance. Colors range from light yellow to almost black. They melt to fluid liquids which darken upon continued heating above their melting points, but decompose only at much higher temperatures. Rapid decomposition of the highest melting grades is reported to occur only at temperatures above about 350°.

Specific gravities lie between 1.08 and 1.15; refractive indices, between 1.617 and 1.650. Dielectric strength at 100° of 150–160° melting grades is about 490 volts per mil in 0.05 inch thickness. Power factor at 60 cycles is 0.5 per cent to 1.0 per cent; at 1500 kilocycles, 0.04 per cent. Specific inductive capacity is 2.42 to 3.45. The dielectric constant is about 2.5. Unfavorable humidity conditions as well as immersion in water and brine do not greatly affect these electrical properties.

Coumarone-indene resins are practically neutral, having an acid number of about 0.5. Being substantially hydrocarbon in nature, they are non-reactive with most chemicals, including alkalies and dilute acids. They are insoluble in the lower mono- and polyhydric alcohols, but soluble in most other organic solvents, including complex and aromatic alcohols, esters, ethers, ketones, aromatic hydrocarbons and hydrogenated naphthas, chlorinated solvents, most fatty oils except castor oil, and such miscellaneous liquids as carbon disulfide, dioxane, aniline, and nitrobenzene. Raw drying oils are better solvents than blown oils. Their solubility in aliphatic hydrocarbons is limited. They are compatible with most plasticizers and blend with many waxes, rubber, chlorinated rubber, synthetic rubbers, most natural resins, modified phenolics, alkyds, methacrylates, and polystyrene. They possess limited compatibility with the vinyl resins, polyisobutylene, and ethyl cellulose and are incompatible with cellulose esters.

Coumarone-indene resins are important components of numerous surface coatings formulated by the paint and varnish industry. They are used in the preparation of printing inks and numerous adhesives. They are employed by the paper industry in boxboard stiffening and paper wax-

ing treatments. They are important binders in the manufacture of alkali-resistant, light-colored mastic floor tile and have become generally accepted by the rubber industry as softeners and tack producers to improve processing properties of both natural and synthetic rubber stocks. They have also found considerable use as a substitute for chicle in chewing gum, sometimes comprising as much as 10 per cent of the total weight of the latter. Numerous miscellaneous applications have been developed, including use as components of putties and caulking compounds, battery boxes, phonograph records, sealing wax, and oil cloth.

Approximately 85 per cent of the total domestic coumarone-indene resin production is normally consumed in the manufacture of floor covering and rubber goods. Approximately ten per cent is utilized in surface coatings.

Coumarone-indene resins are produced in numerous grades under the trade names "Cumar," "Nevindene," "Neville Resin," "Paradene," "Nuba" (a resinous pitch), and "Piccoumaron." Some 30,000,000 pounds of these resins were made in the United States during 1941 at prices ranging from 3 to 14 cents per pound, depending on the grade. The coumarone-indene resins are one of the cheapest types of all synthetic resins currently available.

Hydrogenated Coumarone-Indene Resins

It has already been shown that the presence of unsaturated end groups in the relatively low molecular weight, hemicolloidal polymers of coumarone and indene is a source of gradual discoloration. Moreover, these resins, even when fresh, are never completely water white. This discoloration has been traced to combined oxidation of the double bond in the side chain and fulvenation of the methylene group of the ultimate cyclopentadiene group. An obvious way to eliminate this trouble is to saturate the double bond of the side chain, at once destroying its reactivity toward oxygen and eliminating the presence of a cyclopentadiene grouping. Recent commercial developments have been directed toward this objective and hydrogenated products made with the use of a Raney nickel catalyst have been sold under the trade name "Nevillite." As would be expected, these compounds sell at a premium. In 1942, prices ranged from 52 cents to \$1.30 per pound, depending upon the degree of hydrogenation and consequent lack of color. The highest priced grades are water white and retain their clarity upon prolonged atmospheric exposure of thin films. The iodine number of these resins is below 16.

Concentrated sulfuric and hydrochloric acids are without effect upon these resins. Concentrated nitric acid produces a surface yellowing. Their solubilities resemble those of the coumarone-indene resins, from which

they are derived, except that they are more readily dissolved by paraffinic hydrocarbons. They are incompatible with vinyl resins and with cellulose nitrate and acetate. On the other hand, they blend well with mineral oils, paraffin and polyisobutylene. They are compatible with certain modified alkyds, polymethyl methacrylate, polystyrene, chlorinated and isomerized rubber, and some of the factices. They are compatible with ethyl cellulose to a limited extent.

Hydrogenated coumarone-indene resins are particularly recommended for light-stable, corrosion-resistant surface coatings in which mineral spirits can be used as the sole thinner. They have been proposed as resinous bases for linings of tin cans serving as food containers.

They have found a specialized, but important outlet in combination with raw rubber in the manufacture of gum masses for application to transparent, pressure-sensitive cellulose tapes.

A particularly high grade product sold under the trade name "Clarite" has found utility in mounting botanical and biological specimens for microscopic examination.

Modified Coumarone-Indene Resins

In recent years, a few modified coumarone-indene resins have appeared on the market. Chief among these products is "Nevillac." This resin is a coumarone-indene polymer in which cresols and xlenols are admixed with the naphtha during polymerization so that the resulting product contains phenolic groups in its structure. It has been assumed that the end group unsaturation of the coumarone-indene polymer is saturated by addition of a phenolic compound across the double bond, to form a mixture of polycoumarone-indene substituted cresols and cresyl ethers. Polymerization is carried out between 90 and 110° with the use of an activated clay catalyst. Viscous, oily condensation products are obtained simultaneously and are removed by combined steam and vacuum distillation.

These phenol modified coumarone-indene resins are available in different grades having melting points ranging from 5 to 95° and in colors varying from light yellow to amber. The average molecular weight of the higher melting products runs from 400 to 440. They are soluble in those liquids which dissolve coumarone-indene resins and are, moreover, completely soluble in alcohol. Their compatibility with oils and other resins is, in general, greater than that of the coumarone-indene resins. In contrast to the latter, they blend with ricinoleic acid and many ricinoleic esters, with bodied castor oil, and with Congo and Kauri gum. They are more compatible with modified alkyds and phenolics and with vinyl resins and cellulose esters than are the coumarone-indene resins. They are incompatible with polyisobutylene and isomerized rubber.

Recommended applications are in nitrocellulose lacquers and other surface coatings. They retard the gelling of tung oil and eliminate gas-checking of tung oil varnishes upon forced drying.

"Phenester" differs from "Nevillac" in that it is a straight coumarone-indene resin having an appreciable content of uncondensed phenols.

In contrast to other coumarone-indene resins, "Neville Resin 465" is slightly alkaline in reaction. It is said to be composed of coumarone-indene polymers combined with metallic soaps of a monobasic alicyclic acid. It is dark brown in color and possesses a melting point range of 110 to 125°. Recommended uses are similar to those of coumarone-indene resins.

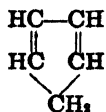
Modified coumarone-indene resins have been prepared by acylation with chlorides of the higher fatty and oily acids. These products do not yet appear to have attained commercial recognition.

Modification of coumarone-indene resins by copolymerization with styrene was once attempted on a commercial scale. The products, known as "Cyrene" resins, seem to have been short-lived.

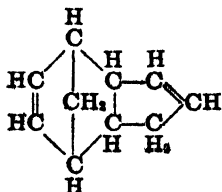
In addition to the materials described above, certain other modified coumarone-indene resins are being produced on a more or less developmental basis. Water dispersible resins of this type are available under the name "Nevilloid," while products designed especially for low temperature flexibility are sold under the name "Nevtex."

Cyclopentadiene Resins

Cyclopentadiene,



is a volatile liquid boiling at about 41°. Upon standing, it readily dimerizes to a solid melting at 32–33° to which the following structure has been assigned in the sense of the Diels-Alder reaction:



Numerous observations have been made upon the polymerization of cyclopentadiene and dicyclopentadiene. A commercial product, marketed under the trade name "Neville G Resin," is apparently produced by copolymerization of dicyclopentadiene, indene, and coumarone occurring together in a grade of naphtha in which these unsaturates are present in the approximate ratio of 60-65 : 15-20 : 5-10. Thermal polymerization is carried out at temperatures above 200°, the molecular weight of the product being in the order of 500 to 600.

"Neville G Resin" is a brittle, dark red solid with a greenish cast melting at 110 to 125°. Its suggested uses are similar to those of the coumarone-indene resins.

Hemicolloidal resins have also been produced from cyclopentadiene by the United Gas Improvement Company. An attempt has been made to adapt them to surface coatings and, particularly, to can linings. Commercialization of these products, however, has lagged.

Occupying a unique position among cyclic unsaturates, cyclopentadiene has been polymerized on numerous occasions to rubber-like materials. Optimum conditions for the formation of cyclopentadiene rubber appear to be low temperature and use of boron trifluoride as a catalyst. Unfortunately, upon standing in the atmosphere, the rubber-like polymer first formed rapidly discolors and becomes hard and brittle. Because of this behavior, which has not been overcome, polymers of this type have found no useful applications as yet.

Cyclopentadiene is an extremely interesting and reactive compound. It possesses polymerizable double bonds; it possesses conjugated diolefinic unsaturation; it possesses an active methylene group capable of undergoing reaction with aldehydes and numerous other compounds. It therefore seems inevitable that this compound, which occurs in the products of coal carbonization will, in the future, find important outlets in the field of synthetic resins and plastics. Its use in the production of alkyd resins through "Carbic" anhydride has already been discussed in Chapter 11.

Terpene Resins

Terpenes have recently become a source of hemicolloidal thermoplastic resins which resemble the coumarone-indenes in physical appearance, properties, and recommended uses. Points of distinction are to be found in their color stability and in some of their solubility and compatibility characteristics.

These resins are available in melting points ranging from 10 to 150°. Molecular weights of 650 and 1600 have been reported. Their density is about 1. They are unsaturated, having a bromine number in the order of

100. They are light yellow in color, but are free from after-yellowing and do not discolor seriously upon long-continued heating. Because of their hydrocarbon character, they possess a maximum acid number of 1 and are resistant to dilute acids and alkalis. They are insoluble in methyl and ethyl alcohols, acetone, and ethyl acetate. They are soluble in most other organic solvents, including petroleum naphthas and mineral oils. They are compatible with numerous waxes and oils, with coumarone, indene and alkyd resins, with rosin, factice, rubber, isomerized rubber, gutta percha, and polyisobutylene. They are not compatible with cellulose esters and ethers, vinyl resins, the methacrylates, polystyrene, "Vinsol," and most phenolics.

They are available under the trade names "Piccolyte" and "Nypene." Prices are in the order of 16 cents per pound.

Hydrogenated water-white terpene resins have been produced experimentally, but are not yet commercial.

Petroleum Resins

The cracking of petroleum, especially vapor-phase cracking, yields gasoline of high anti-knock value which possesses an appreciable amount of readily polymerizable unsaturates that must be removed in order to stabilize it.

Although the nature of these hydrocarbons is very complex and not clearly defined, some experimental work has been carried out, for orientation purposes, upon pure aliphatic unsaturates. It has been found that pure isoprene does not polymerize appreciably in the presence of aluminum chloride. Addition of pentene-2, however, causes immediate polymerization with formation of two different types of polymers, the one insoluble, the other soluble. The former appears to be a polymer of isoprene alone, the latter a copolymer of the olefin and diolefin. The yield of soluble polymer increases while the yield of insoluble polymer decreases with increasing amounts of pentene-2. The insoluble polymer can be converted to a soluble form by heating at 300° out of contact with the air. Isoprene also yields resinous products upon condensation with alkylated benzenes, although benzene itself does not give rise to resins under the same conditions. Cyclic olefins and diolefins behave in a manner similar to their acyclic analogs.

These observations have been applied in the controlled polymerization with aluminum chloride of carefully selected, highly unsaturated cracked petroleum distillates. A typical grade of this material is translucent in thick layers and reddish-amber in color. It melts at 93-94° and has an acid number of 0.1. Its iodine number runs from 125 to 135.

These resins are soluble in hydrocarbon solvents, both aliphatic and

aromatic, in turpentine, and drying oils. They increase the speed of drying of tung oil. They are insoluble in methyl and ethyl alcohol, acetone, and ethyl acetate, but are soluble in higher acetates.

The degree of unsaturation of these resins can be altered by varying the proportion of catalyst used, as shown by Figure 117. The more highly

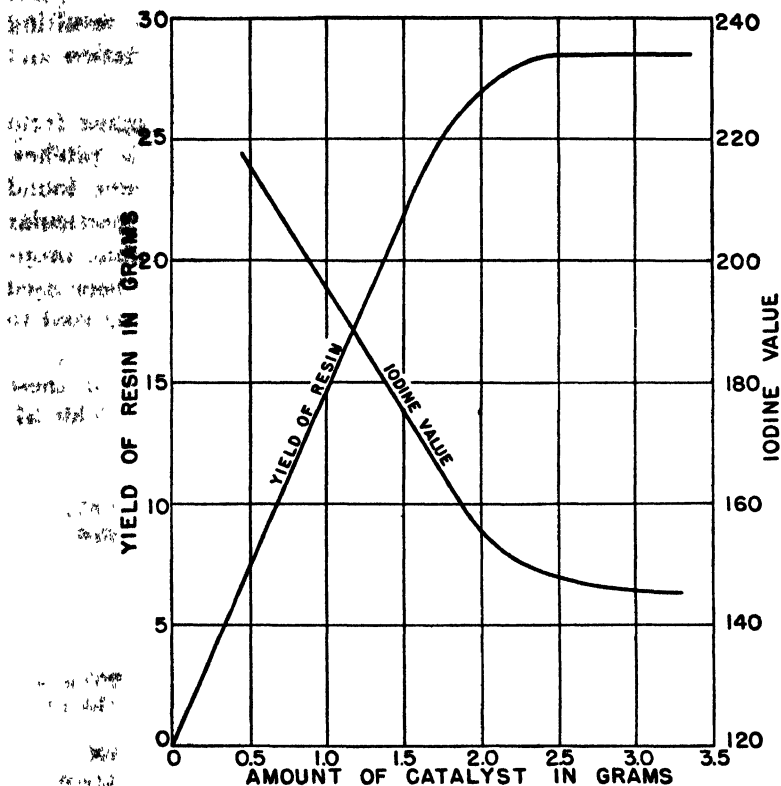


Figure 117. Effect of aluminum chloride catalyst on iodine value and yield of resin from highly cracked petroleum distillate. (Resin yield and catalyst expressed in grams per 100 cc. of distillate.) (Thomas and Carmody¹⁹)

unsaturated resins dry upon baking so that films deposited from petroleum solvents become insoluble in the original solvent after heating for an hour at 105°.

Formerly known as "Santo" resins, these products were once offered to the trade at 15 cents per pound in carload lots. Their production, however, has now ceased.

The "polymer slop" obtained as a by-product in the refining of vapor phase gasoline is a source of cheap, low-grade resins. The principal char-

acter of the reactive hydrocarbons responsible for their formation appears to be cyclic, non-conjugated, and diolefinic. These unsaturates are removed from the gasoline by polymerization to viscous materials which still possess sufficient unsaturation to absorb oxygen and dry readily upon exposure in film form to the atmosphere. Although normally thermoplastic, films of these resinous materials baked in the absence of oxygen are capable of undergoing further polymerization, presumably resulting in cross-linked, tridimensional, thermoset structures. Both oxidation and polymerization are accelerated by conventional driers.

Vacuum distillation of polymer slops yields substances ranging from light-colored volatile liquids to dark, viscous, non-distillable pitches. They are compatible with drying oils and most resins and have found utility in the formulation of surface coatings. They are of particular merit as aluminum vehicles because they possess excellent leading properties. They are also valuable anti-skinning agents. They have been used in core oils, as binders for rock-wool insulation, and in spraying coal to minimize dusting and increase B.t.u. content.

Physical and chemical properties of three different grades of these resins, marketed under the trade name "Petropol" are listed in Table 37.

Table 37. Physical Properties of Some Commercial "Petropols" ¹⁰

Specific gravity 60° F/60° F	0.9497	0.9923	1.925
Gravity, ° A.P.I.	17.6	11.14	10.0
Flash, C.O.C.	175° F	230° F	
Fire, C.O.C.	215° F	280° F	
Viscosity, Saybolt Univ.			
At 100° F	200-225		
At 210° F		225-300	
Iodine number	195 min	200 min	300 min
Melting point			170-190° F
Pour point	0° F	+ 45° F	
Per cent solids	60-65	90-92	100
Saponification number	Trace	Trace	Trace
Unsaturation, %	99 +	99 +	99 +
Asphaltic compounds, %	0.11	0.16	0.2
Paraffin	None	Trace	Trace
Molecular weight	300	425	700
% Ash	0.005	0.012	0.02

Soluble in —

Mineral spirits, benzene, toluene, xylene, ethyl alcohol

Resistant to —

Water, acids, alkalis

The lowest grade "Petropols" are among the cheapest commercial resins, selling from 2 to 5 cents per pound in tank car lots.

Of somewhat similar origin and nature is "Naftolen," available in various grades as a reddish-brown liquid of the consistency of cold

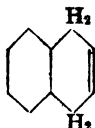
Its average molecular weight is about 400, its iodine number about 40, and its acid number 0. It is widely compatible with oils, resins, and elastomers, and is especially recommended as a vulcanizable plasticizer for natural and synthetic rubbers, with the exception of "Thiokol."

Many other resins are potentially available from petroleum by extraction of naturally occurring asphaltenes, as a result of various processing operations, and by chemical syntheses such as condensation with formaldehyde or chlorination followed by dehydrohalogenation. Little success, however, has as yet been achieved in the utilization of such resins.

Hydronaphthalene Resins

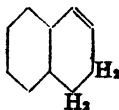
An interesting series of resins prepared by polymerization of dihydronaphthalenes has been described. Some of these products have in times past provoked commercial interest to a limited extent. They are, however, not currently available.

By reduction of naphthalene with sodium and ethyl alcohol at temperatures in the order of 80°, 1,4-dihydronaphthalene,



is obtained. The same compound is produced by reaction of water with sodium naphthalene dissolved in a suitable solvent, such as dimethyl glycol ether, at temperatures below - 30°. Sodium naphthalene $C_{10}H_8Na_2$, in turn, is obtained by reacting metallic sodium with naphthalene dissolved in dimethyl ether or glycol diethers.

If the reduction of naphthalene with sodium and ethyl alcohol is carried out at temperatures of 150°, 1,2-dihydronaphthalene,



is produced. It can also be obtained by quantitative rearrangement of the 1,4-isomer by heating the latter with a 10 per cent alcoholic solution of sodium ethylate for 3 to 4 hours at 150°.

Both 1,2-dihydronaphthalene and 1,4-dihydronaphthalene can be polymerized in dimethyl glycol ether solution by the catalytic action of sodium naphthalene. Mixtures of the two isomers can also be copolymerized.

By polymerization of the 1,2-isomer at temperatures below - 80°, a colorless, amorphous powder is obtained which gives no appearance of softening at 250° and which chars only slightly below red heat. It is

insoluble in most organic solvents and appears to possess a very high molecular weight. Polymerization at higher temperatures yields similar products having greater solubility.

1,4-Dihydronaphthalene polymerizes slowly by the catalytic influence of appreciable amounts of sodium naphthalene. The reaction requires several hours for completion at room temperature and some 50 hours at 0°. The product is a brittle, water-white, glass-like, thermoplastic resin. It melts to a limpid fluid upon heating, its melting point rising as the temperature of polymerization is lowered.

The polymer of 1,4-dihydronaphthalene obtained by polymerization at room temperature softens below 100° and becomes completely fluid at 110–120°. It has an average molecular weight of 400 to 450. Cracking does not occur below 370°. The resin is water-white and shows rather good color retention, although upon long standing it does yellow. Color stability is improved by hydrogenation, an operation which simultaneously causes a 30 to 40° increase of melting point.

This resin has a specific gravity of 1.14, a refractive index at 24° of 1.60, a dielectric constant at 25° and 1000 cycles of 3.0, and an approximate power factor at 25° and 1000 cycles of 0.002. It is neutral and resistant to acids and alkalis. Its solubilities are as follows: insoluble in water, methanol, ethanol, and glycerol; slightly soluble in acetone, ethyl acetate, and ethyl "Cellosolve"; moderately soluble in gasoline, isopropyl ether, and cyclohexanone; very soluble in turpentine, aromatic hydrocarbons, chlorinated solvents, and carbon disulfide. It is compatible with drying oils, asphalt, rosin, polystyrene, and polyvinyl chloride. It possesses limited compatibility with paraffin, beeswax, and stearic acid.

Condensation Products of Aromatic Hydrocarbons and Formaldehyde

The Nastukoff reaction, whereby amorphous solids are obtained by reaction of formaldehyde with unsaturated hydrocarbons in the presence of sulfuric acid, has been extended to the production of resinous condensation products from aromatic hydrocarbons in general, as witnessed by United States Patents, Nos. 2,200,762–3. In particular, naphthalene can be condensed with formaldehyde in the presence of sulfuric acid to yield friable resins resembling polycoumarone-indene in physical appearance. Although these resins have been investigated in both England and the United States, they have not yet attained commercial recognition.

"AXF"

Falling in the category of miscellaneous hydrocarbon resins is a product known as "AXF," introduced in 1935 as a compounding ingredient for use

with natural and synthetic rubbers to increase oil and gasoline resistance. This substance is described as an elastic plastic produced by the reaction of an ethylene dihalide with an aromatic hydrocarbon of the general formula $R-C_6H_4-R'$, where R and R' are hydrogen atoms or saturated alkyl groups containing two or more carbon atoms. Toluene and xylene are said to be unsuitable for this reaction. Condensation is carried out by means of aluminum chloride.

"AXF" does not react with sulfur. It swells only slightly in ethanol, acetone, gasoline, kerosene, and light lubricating oils. After immersion in spindle oil for five days at 70°, it shows a volume increase of less than 4 per cent.

General physical and chemical properties of "AXF" are listed below in Table 38.

Table 38. Properties of "AXF" ¹⁸

Specific gravity	1.04
Ash, per cent	1.2
Color	Dark brown
Odor	Practically none
Hardening temp., °C	0
Tensile strength, lb/sq in	Up to 450
Elongation, per cent	Up to 600
Action of acids and alkalis after immersion for one week at room temp.:	
Conc. HCl	No action
Conc. H ₂ SO ₄	Swells and hardens slightly
50% H ₂ SO ₄	No action
Conc. HNO ₃	Attacked slowly
Glacial HOAc	Swells moderately
50% NaOH	No action
NH ₄ OH(30% NH ₃)	Surface bleached

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Chapter 14

Vinyl Resins

The vinyl resins are among the oldest polymers known to chemical science, but their industrial development has occurred almost entirely during the past two decades. Indeed, before the outbreak of World War II they were still almost in a state of infancy. Since 1941, however, they have dramatically stepped into rank among the most versatile and most rapidly expanding groups of commercial plastics. Today they are one of the five major families which make up the bulk of domestic production in the plastics industry.

The raw materials from which they are derived—petroleum, natural gas, coal, limestone, air, water, and brine—are cheap and abundant, so that current enlarged production facilities augur well for their future place among relatively low-cost resins. They are available in a great profusion of chemical modifications and physical forms, both of which are constantly increasing in number. Their applications are legion.

HISTORY

Discovery of the first vinyl resin has commonly been accredited to the Frenchman, Regnault. In 1835 he synthesized vinyl chloride, but there is no record that he observed its polymerization. Three years later, however, he did produce polyvinylidene chloride, a closely related type of resin to be discussed in Chapter 15.

In 1860, while working in London, A. W. Hofmann carried out the earliest recorded preparation of a true vinyl polymer—the polybromide. Twelve years after that, E. Baumann reported its synthesis again, together with that of polyvinyl chloride, and studied both of these products in some detail.

Modern interest in the polymerization of vinyl halides was revived by the Russian chemist, Ostromislensky, who later came to the United States where he continued work in this and many other fields. In 1912, he obtained the earliest patents on vinyl polymers. Coincidentally, vinyl acetate was prepared and polymerized by the German, Klatte, who observed the catalytic influence on its polymerization of such compounds

as benzoyl peroxide. Monomeric vinyl acetate had been produced in an impure state as early as 1860 by the Russian chemist, Miasnikoff, but neither its physical properties nor its tendency to polymerize were recorded at that time. This compound was produced in Canada in 1917, but no important commercial applications of vinyl resins occurred until some ten years later.

Research in this field was intensified after World War I, however, and many scientific articles, as well as numerous patents, appeared during the following decade. It was found that the hard and horny straight polymers of vinyl chloride are difficult to fabricate into useful articles and cannot be plasticized by admixture with the much softer polyvinyl acetates with which they are incompatible. During the 'twenties, however, E. W. Reid observed that polyvinyl chloride could be made much more amenable to mechanical manipulation by internal plasticization with vinyl acetate as the result of copolymerizing the two monomers—chloride and acetate. Following this discovery, vinyl chloride-acetate copolymer resins were developed by the Carbide and Carbon Chemicals Corporation and sold under the trade-mark "Vinylite." Such copolymers were first manufactured by this company in 1927, but large-scale production did not begin until 1933. In the latter year, an experimental house, built by the Pierce Foundation in cooperation with Carbide, was constructed of vinyl polymers and equipped with articles made therefrom. This harbinger of vinyl plastics was displayed at the Chicago World's Fair and afforded a remarkable prophecy of many of the different ways in which these resins have since been fabricated on an industrial scale.

Other producers entered the field. Shawinigan Chemicals, Ltd., was one of the earliest. In 1932 this firm completed erection of a vinyl acetate plant having a daily capacity of two tons. Experimental and large-scale production of polyvinyl acetals soon followed and paved the way for subsequent developments in the field of safety glass.

The du Pont Company later introduced polyvinyl alcohol as an industrial chemical and, still later, began the production of polyvinyl acetate emulsions, now also manufactured by Shawinigan and others.

Although dwarfed by wartime production of vinyl wire and cable coating, what was then a spectacular rise for a member of the vinyl family occurred in 1936 when polyvinyl butyral was evolved as the interlayer for high-test safety glass. Developed by the Carbide and Carbon Chemicals Corporation in collaboration with the Pittsburgh Plate Glass Company, this resin was in fact a practical outgrowth of Shawinigan's earlier and more theoretical studies of polyvinyl acetals in general. Butyral manufacture was first undertaken on a commercial scale by Carbide, Shawinigan, and Monsanto, then by du Pont. The plastic gained in favor so

rapidly that, by the time automobile construction was halted after Pearl Harbor, it was being used in practically all of the safety glass made in this country.

Late in the 'twenties, during the course of a search for methods of bonding rubber to steel, Waldo L. Semon of the B. F. Goodrich Company recognized the rubber-like qualities of properly plasticized polyvinyl chloride which, in a few years, was placed on the market in molded and extruded shapes—especially sheet and tubing—under the trade-mark "Koroseal." Fabrics coated with this material were developed later. About 1940, Goodrich began their own manufacture of polyvinyl chloride, using acetylene as raw material.

During the decade of the 'thirties a remarkable series of developments occurred in "Vinylite" copolymer resins. In 1933, the so-called "Keg-lined" beer can appeared. Use of a vinyl lacquer as a tin can liner was a fore-runner of important developments in the field of surface coatings. The widespread adoption of vinyl resins for such purposes was long delayed because of difficulties in application, but recent developments in large-volume production of low-cost ketones have overcome many of these problems. Indeed, the use of vinyl resins in surface coatings which has followed large-scale commercial manufacture of ketones during the past decade parallels, to some extent, the earlier growth of pyroxylin lacquers made possible by the introduction of unlimited volumes of inexpensive ester-type solvents after World War I.

The versatility of vinyl copolymer resins has been repeatedly demonstrated by the appearance in rapid succession of rigid sheets in 1937-38, flexible sheeting in 1939-40, and "Vinyon" textile fiber in 1939. The so-called "Plastisols" and "Organosols," based on vinyl resins and introduced in 1944, have opened new vistas in low-pressure, low-cost molding and coating techniques.

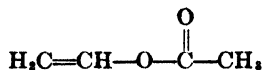
Vinyl resins have proved invaluable to the Army and Navy. Although utilized in many different ways by the armed forces, their largest single military use has been in wire and cable coatings. It is chiefly this application which has accounted for their great increase in production since 1941. Water-proofing of cloth has been another essential wartime use. For these and other purposes, the trend in recent years has been toward increased use of highly plasticized polymers and copolymers containing a large percentage of vinyl chloride and possessing high molecular weights.

Current domestic production of vinyl resins is in excess of 5,000 tons per month. According to U. S. Tariff Commission figures, total 1944 volume of polyvinyl alcohol, ester, and chloride resins was 111,900,000 pounds, averaging 43 cents in unit value. Production of polyvinyl acetals was 14,992,000 pounds, with unit value of 90 cents.

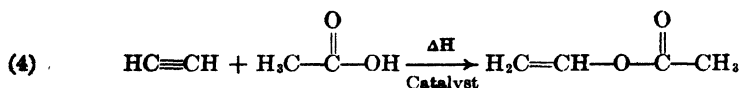
pany in a complementary manner, hydrogen chloride produced by catalytic dehydrohalogenation of ethylene dichloride being reacted with acetylene.

Vinyl Acetate

Vinyl acetate

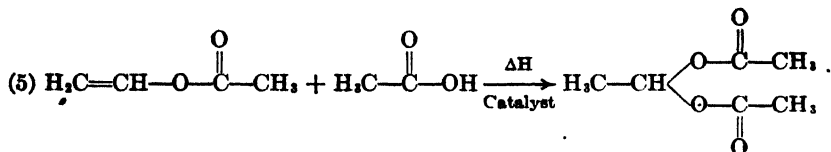


is a volatile liquid which boils at 73° and possesses an odor reminiscent of acetaldehyde, although more sweet. It is obtained by direct addition of acetic acid to acetylene at slightly elevated temperatures (40–50°) in the presence of a suitable catalyst:



While many substances exercise a catalytic influence upon this reaction, the acidic salt prepared by action of excess acetyl sulfuric acid upon mercuric oxide is particularly effective and is used industrially to the extent of some 2 per cent by weight of the acetic acid. Acetyl sulfuric acid is prepared by passing sulfur trioxide into glacial acetic acid or by addition of oleum to mixed acetic acid and acetic anhydride at temperatures below 70°. Above this temperature, acetyl sulfuric acid is transformed into less active sulfoacetic acid.

By further reaction of vinyl acetate with acetic acid in the presence of the same catalyst, ethylidene diacetate is produced:

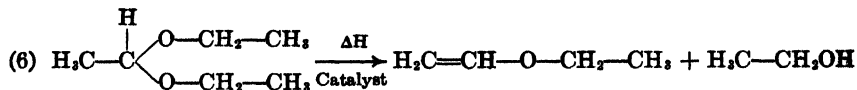


The factors that determine the extent to which reaction (5) occurs are principally temperature and extent of removal of vinyl acetate from the sphere of reaction. The higher the temperature and the more complete the return of vinyl acetate to the reaction mixture by reflux, the greater is the yield of ethylidene diacetate with respect to vinyl acetate. High yields of vinyl acetate with correspondingly low formation of ethylidene diacetate can be obtained by use of a mercuric phosphate catalyst.

It will be recalled that pyrolysis of ethylidene diacetate yields acetic anhydride, essential to the production of cellulose acetate. This relationship between two quite different families of plastics is noteworthy.

Vinyl Ethers

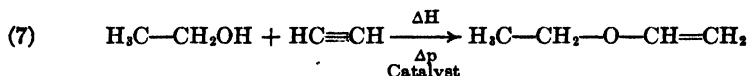
Several laboratory methods are known for the preparation of vinyl ethers, but the earliest practicable process of industrial merit involved catalytic decomposition of saturated acetals in the vapor phase:



This process is still favored in current American developments.

Divinyl ether was at one time produced domestically, apparently from dichloroethyl ether, and sold as an anaesthetic under the name, "Vinethene."

Modern German practice has utilized acetylene as the essential intermediate for vinyl ethers, an alcohol being added directly across the triple bond under suitable catalytic influence:



Several chemicals are capable of acting as catalysts for equation (7). The corresponding sodium alkylate has been used industrially abroad. Reaction is carried out at 150° under pressures of 15 to 30 atmospheres.

Table 39 lists properties of several monomeric vinyl ethers.

Table 39. Physical Constants of Certain Monomeric Vinyl Ethers²⁸

Ether	Formula	Boiling Pt. °C (corr.)
Vinyl methyl	$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$	(gas) 12-14
Vinyl ethyl	$\text{CH}_2=\text{CH}-\text{O}-\text{C}_2\text{H}_5$	35.5
Vinyl <i>n</i> -butyl	$\text{CH}_2=\text{CH}-\text{O}-\text{C}_4\text{H}_9$	93.3
Vinyl <i>beta</i> -chloro-ethyl	$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$	108.0
Vinyl phenyl	$\text{CH}_2=\text{CH}-\text{O}-\text{C}_6\text{H}_5$	155.5

Ether	Density D_4^{20}	Refractive Index	M_D Found	M_D^* Theor.
Vinyl methyl				
Vinyl ethyl	0.7723 (D_4^{20})	1.3856 (n_D^{20})	21.89	21.85
	0.7589			
Vinyl <i>n</i> -butyl	0.7887	1.4026 (n_D^{20})	30.94	31.08
Vinyl <i>beta</i> -chloro-ethyl	1.044	1.4362 (n_D^{20})	26.65	26.71
Vinyl phenyl	0.9776	1.5226 (n_D^{20})	37.49	36.72

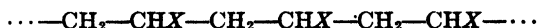
* Calculated from the atomic refractivities given by Eisenlohr and V. Auwers, *Z. physik. Chem.*, **75**, 585-607 (1911).

POLYMERIZATION OF VINYL MONOMERS

Monomeric vinyl compounds can readily be converted to an almost unlimited number of polymers and copolymers varying in average molecular weight and, in the case of copolymers, in the ratio of different

monomeric units present in each macromolecule. The same fundamental principles apply to the formation of all these polymers. Moreover, many of the relations which exist among reaction conditions, molecular weight, and rate of polymerization can be generalized to apply to numerous thermoplastics derived from other monomers containing vinyl or vinylidene radicals such as styrene, methyl methacrylate, and vinylidene chloride. In general, the formation of polymers from vinyl compounds is thought to be the result of chain reactions.

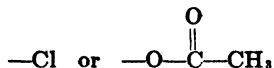
The large molecules thus produced appear to possess a "head-to-tail" arrangement of their unit groups, so that their structure may be represented by the general formula:



or, less adequately:



where n is the degree of polymerization. In the case of most of the primary vinyl resins discussed in this chapter, obtained by direct polymerization, X is usually



or both. The degree of polymerization, n , may range from 20 to over 3000.

It should be noted that molecular weights reported for commercial vinyl polymers have ordinarily been determined by means of viscosimetric methods. Even in dilute solutions, however, Staudinger's relationship is inaccurate and consistent results are difficult to obtain, so that apparent molecular weights measured by viscosimetry may be in error by as much as 500 per cent or even more. Most of the values given in the literature for commercial products are far too low.

Industrial Polymerization Processes

There are three principal methods by which unsaturated compounds are polymerized on an industrial scale. They are (1) bulk, (2) bead, and (3) emulsion processes. In bulk polymerization, the monomer is resinified directly, either in the presence or absence of solvent, by addition of an appropriate catalyst and, usually, by application of heat. The temperature of polymerization—a critical factor in the determination of molecular weight—can often be conveniently controlled by carrying out reaction at the boiling-point of a suitably selected solvent or solvent mixture which need not necessarily dissolve the polymer. If the liquid used to dilute the monomer is a non-solvent for the resin produced there-

from, the latter is precipitated as rapidly as it is formed. Bulk methods of polymerization are used industrially not only in the manufacture of vinyl polymers and copolymers discussed in this chapter, but also in the production of commercial polymers of styrene, methyl methacrylate, isobutylene, and other unsaturates such as coumarone-indene mixtures.

In bead or granulation methods of polymerization, a fine stream of monomer is run into a bath consisting of an immiscible fluid—water in practice—which contains a suitable catalyst and colloidal substance such as gelatin, methyl cellulose, hydroxyethyl cellulose, or polyvinyl alcohol. Reaction is effected while carrying out such vigorous agitation that the current of monomer is whipped up into droplets that are suspended in the colloidal dispersion and converted into granules of polymer. The product is often sufficiently finely divided for direct use as a molding material. Granulation methods are especially favored in the production of polymethyl methacrylate molding powders and are used by certain manufacturers in the polymerization of vinyl acetate.

Emulsion polymerization is carried out by dispersing the monomer in an immiscible liquid—again water, in practice—by means of an emulsifying agent and bringing about polymerization by addition of a catalyst, usually a water-soluble peroxygen compound like sodium perborate. The use of emulsion polymerization methods *par excellence* is in the manufacture of synthetic rubbers, most of which are now made in this way. Some concerns produce polyvinyl acetate and polyvinyl chloride by emulsion methods. Other thermoplastics, such as polystyrene, are also obtained by emulsion polymerization. As noted in the next section, this type of process can be carried out with less careful control than bulk operations.

Factors Influencing Polymerization

Polymerization of vinyl esters is accelerated by light, heat, and catalysts. Both the average molecular weight of the polymer and the rate of its formation are determined, in part, by these factors. The presence of certain impurities, even in traces, may accelerate, inhibit, or alter the course of polymerization. Where reaction is carried out in solution, both the concentration and specific nature of the solvent exercise an influence.

In photopolymerization, the extreme ultraviolet is most effective, but catalysts like salts of uranium, cobalt, vanadium, and lead cause visible light to become active.

Thermal polymerization of vinyl esters is catalyzed by ozone, by peroxides, such as benzoyl peroxide, lauroyl peroxide, and *ter*-butyl hydrogen peroxide, and by metal alkyls like lead tetraethyl. The higher the temperature and the greater the concentration of catalyst, the lower

is the molecular weight of the polymer. Polymerization of vinyl compounds is highly exothermic. Use of an aqueous medium in emulsion polymerization ensures a large body of inert fluid which removes heat rapidly from the individual minute areas of reaction. Hence temperature control can be maintained without painstaking care and high molecular weight products can often be obtained with greater ease than by bulk methods.

Polymerization of vinyl esters is very sensitive to traces of certain impurities. The presence of small amounts of acetaldehyde in vinyl acetate, for example, lowers the molecular weight of the polymer, as illustrated in Table 40, and impairs its light stability.

Table 40. Effect of Traces of Acetaldehyde during Polymerization upon the Viscosity of Polyvinyl Acetate ¹⁰

Acetaldehyde Content (%)	Viscosity Polyvinyl Acetate (cps.)
0.1	20
0.2	15
0.6	6

Reaction conditions: 60 parts vinyl acetate, 40 parts benzene, 0.09 parts catalyst. Refluxed at 73–76° during 4½ hours. Per cent conversion: 66–70.

Sulfur and salts of copper inhibit the polymerization of vinyl esters. Indeed, copper salts are utilized industrially to permit storage and shipment of monomeric vinyl acetate. Subsequent purification can be carried out by simple distillation.

The remarkable specific effect of solvent upon the polymerization of vinyl esters is illustrated by Table 41, showing the molecular weight of polyvinyl acetate produced in different solvents under otherwise substantially identical reaction conditions.

Table 41. Effect of Specific Solvent upon the Polymerization of Vinyl Acetate ¹⁰

Solvent	% Conversion	Molar Viscosity of Polymer in Benzene Solution (cps.)
Toluene	29.0	2.9
Acetone	68.5	3.0
Absolute alcohol	22.6	5.6
Acetic acid	78.7	6.8
Ethyl acetate	89.3	8.2
Benzene	55.0	18.2

Reaction conditions: Ratio of vinyl acetate to solvent: 1/1.
Catalyst: 0.2 per cent of weight of monomer. Temperature: 78°.

The greater the concentration of monomer in a given solvent, the higher is the molecular weight of the polymer other conditions being held

constant. The molar viscosity of polyvinyl acetate, for example, produced in ethyl acetate solution, drops from 18.4 to 8.8 cps as the vinyl acetate concentration is decreased from 60 to 50 per cent. The highest viscosity polymers are obtained in the absence of solvent or in aqueous emulsion.

The rate of polymerization of vinyl esters is likewise affected by the same factors which influence molecular weight. For every 8° rise in temperature, for example, the speed of reaction increases twofold. It also increases with the amount of catalyst, being approximately proportional to the square root of the concentration of the latter. It likewise increases with the concentration of monomer in solution and is specifically affected by the individual solvent. Impurities may also influence the rate of polymerization. Acetaldehyde, for example, accelerates resinification of vinyl acetate, despite its deleterious action on the properties of the polymer. The same effect is noted with water in the presence of alkali, although water alone has little influence. It has been suggested that the catalytic activity of traces of moist alkali is the result of hydrolysis of a small amount of vinyl acetate to vinyl alcohol which immediately tautomerizes to acetaldehyde.

Molecular Weight Distribution in Vinyl Polymers

Polymerization of vinyl compounds never leads to formation of an individual molecular species, but rather to a complex mixture of structurally similar products of varying molecular weight. It has been shown in Chapter 4 that adequate information concerning the degree of polymerization of high polymers can be obtained only from molecular weight distribution curves. Figure 10 of that chapter shows such curves for commercial samples of polyvinyl acetate.

By fractional precipitation of an acetone solution with isopropanol, Douglas and Stoops carried out molecular weight distribution studies upon vinyl chloride-acetate copolymers. Separation into six fractions, or polymer bands, of a copolymer possessing an average apparent molecular weight of 10,600 and a vinyl chloride content of 86 per cent was followed by examination of the physical properties of each band. This study showed that above 5000, molecular weight exercised little influence upon water absorption, heat resistance, refractive index, specific gravity, electrical properties, or hardness of the fractions. On the other hand, there was marked dependence of strength characteristics upon the degree of polymerization. Table 42 and Figures 118, 119 and 120 illustrate several of these relationships in the case of this particular sample of fractionated copolymer resin.

It should be emphasized, however, that in commercial practice frac-

Table 42. Physical Properties of Vinyl Chloride-Acetate Resin Fractions ⁴⁰

	Original Resin	A	B	C	Fraction D	E	F
Mol. weight	10,600	15,800	14,600	13,200	11,100	7,500	5,800
Vinyl chloride content, %	85.9	86.4	86.6	85.7	83.1	84.8	83.9
Refractive index	1.526	1.530	1.526	1.524	1.523	1.523	1.524
Brinnell hardness No. at 2.5-kg (5.5-lb) load	14.2	13.9	13.5	13.2	12.7	12.2	Fractured
Water absorption at 60° (140° F), % gain in wt.:							
18 hr	0.39	0.27	0.40	0.37	0.31	0.29	0.34
168 hr	1.30	0.44	0.47	0.78	0.56	0.54	0.86
Heat distortion point:							
° C	58	64	65	63	66	63.5	62
° F	136.4	147.2	149	145.4	150.8	146.3	143.6
Viscosity of 20 per cent soln. in methyl isobutyl ketone, centipoises	190	Gel	Gel	370	145	45	24
Plasticity at 120° (248° F) by Scott plastometer, %	76	39	52	66	82	94	Could not mold
Tensile strength, lb/sq in	9,052	9,955	9,745	9,630	9,180	6,680	1,120
Impact strength, ft-lb/piece	0.25	0.36	0.33	0.32	0.31	0.16	Could not mold
Fatigue resistance at 2400 lb/sq in, cycles	26,000	940,000	1,000,000	1,000,000	360,000	18,000	Could not mold
Modulus of elasticity, lb/sq in	400,000	418,000	407,000	401,000	403,000	394,000	350,000
Modulus of rupture, lb/sq in	13,300	14,400	14,600	13,000	13,500	9,100	1,470

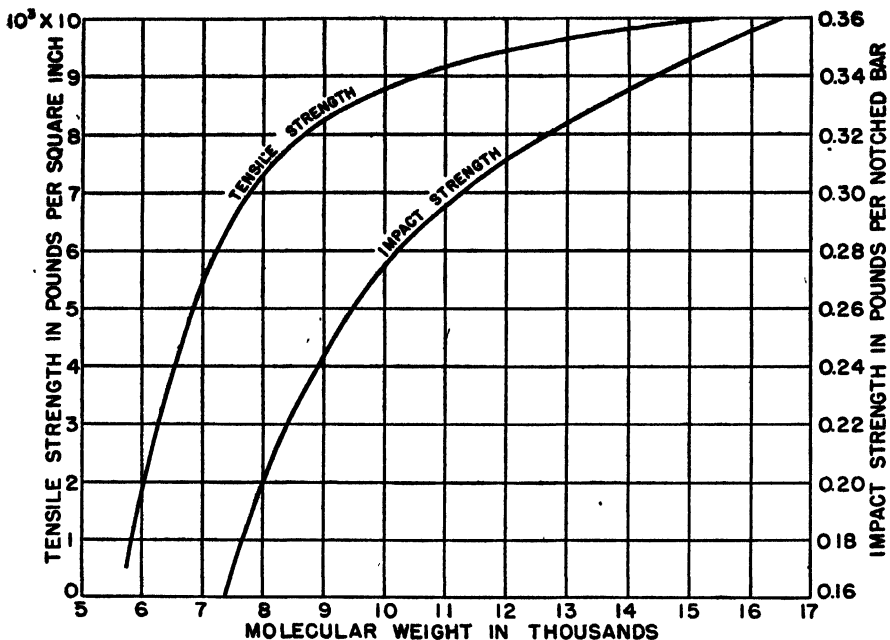


Figure-118. Relation of tensile strength and impact strength ($\frac{1}{2} \times \frac{1}{2} \times 2\frac{1}{2}$ inch notched bars) to molecular weight of vinyl chloride-acetate resin (see Fig. 120).

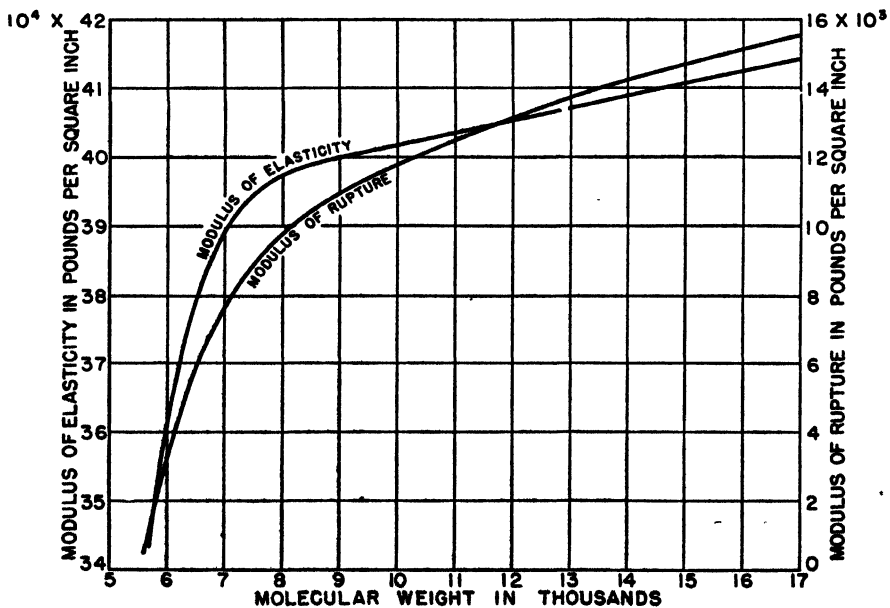


Figure 119. Relation of modulus of elasticity and modulus of rupture to molecular weight of vinyl chloride-acetate resin (see Fig. 120).

tionation is never carried out because of the large-scale difficulties involved and because of the cost of the operation. As close control as possible of molecular weight and molecular weight distribution is established over industrial products by careful adherence to precise conditions of polymerization.

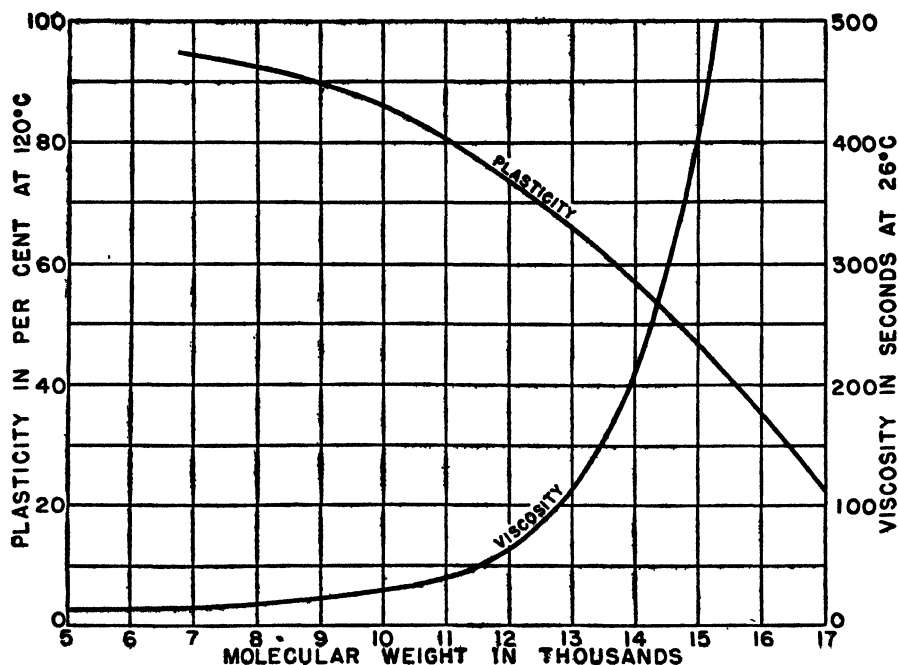


Figure 120. Relation of plasticity (Scott plastometer) and viscosity (20 per cent solution in hexone, Ford cup, No. 4 tip) to molecular weight of polymer bands fractionated from vinyl chloride-acetate resin of 85.9 per cent vinyl chloride content and 10,600 average apparent molecular weight (as determined by the Staudinger viscosity method, using a K_m value of 3.4×10^{-4}). (Curme and Douglas³⁵ See also Douglas and Stoops⁴⁰)

VINYL POLYMERS: COMMERCIAL PRODUCTS

All vinyl resins currently manufactured are thermoplastic. They may be grouped as *primary* or *secondary*, depending upon their method of production.

Primary resins are obtained by direct polymerization or copolymerization of monomeric vinyl compounds. They include principally polymers and copolymers of vinyl chloride, vinyl acetate, and vinyl ethers.

Secondary resins are derived from primary polymers, particularly from polyvinyl acetate, by such metathetical reactions as hydrolysis and acetalation.

The resins discussed in this chapter can be classified as follows:

(A) Primary Vinyl Resins

I. Polymers of vinyl chloride and copolymers of vinyl chloride and vinyl acetate

(a) Hard resins containing more than 95 per cent of vinyl chloride

(b) Soft resins containing less than 92 per cent of vinyl chloride

(1) Tripolymers of vinyl chloride, vinyl acetate, and maleic anhydride

II. Miscellaneous vinyl chloride resins

III. Polyvinyl acetates

IV. Polyvinyl ethers

(B) Secondary Vinyl Resins

I. Polyvinyl alcohol and partially hydrolyzed polyvinyl acetates

II. Polyvinyl acetals

(a) Polyvinyl formal

(b) Polyvinyl acetal

(c) Polyvinyl butyral

Primary Resins

Vinyl Chloride Polymers and Copolymers

Among primary vinyl resins, polyvinyl chloride stands in marked contrast to polyvinyl acetate. The former is a hard, horny substance, insoluble in most organic solvents, except nitrobenzene and cyclic ketones, while the latter is a soft material which melts at relatively low temperatures and dissolves in a wide variety of common organic solvents such as alcohols, esters, ketones, and chlorinated hydrocarbons. Polyvinyl chloride and polyvinyl acetate are incompatible and their mixtures do not, therefore, give rise to useful products. The former, however, can be internally plasticized by copolymerization of vinyl chloride with vinyl acetate. The copolymers can be handled on such machinery as calendars and tubers more readily than polyvinyl chloride itself, as little as 0.5 per cent of acetate exercising a noticeable effect upon ease of fabrication. Facility of plasticization is also markedly improved in copolymers. As the amount of vinyl acetate is increased, the softening point is lowered and ease of plasticization, solubility in organic solvents, and facility of mechanical manipulation and of bonding are increased. Table 43 shows the relation between solubility and composition of certain primary resins derived from vinyl chloride and vinyl acetate.

Table 43. Qualitative Solubilities of "Vinylite" Resins *

	Copolymers of Vinyl Chloride and Vinyl Acetate Containing 85-88% Vinyl Chloride ⁽¹⁾							
	Polyvinyl Acetate ⁽⁴⁾		Polyvinyl Chloride ⁽⁵⁾		Low Molecular Wt. ⁽⁶⁾		Medium Molecular Wt. ⁽⁷⁾	
	25°	95° ⁽²⁾	25°	95° ⁽²⁾	25°	95° ⁽²⁾	25°	95° ⁽²⁾
Acetone	S	S	I	SW	S	S	S	S
Acetonylacetone	S	S	S	S	S	S	S	S
Butanol	G	S	I	I	I	I	I	I
Butyl Acetate (98%)	S	S	S-CL	S-CL	S	S	S	S
"Carbitol" Acetate	S	S	I	I	S	S	S	S
Carbon Tetrachloride	S-CL	S	I	I	I	I	I	I
"Cellosolve" Solvent	S	S	I	I	I	I	S-CL	S
"Cellosolve" Acetate	S	S	I	SW	S	S	S	S
Cyclohexanone	S	S	S	S	S	S	S	S
Diacetone Alcohol	S	S	I	SW	G	S	S	S
Dibutyl Phthalate ⁽³⁾	S	S	PS	S	S	S	S	S
Dichlorethyl Ether	S	S	PS	S	S	S	S	S
Diisobutyl Ketone	I	SO	PS	S-CL	S	S	S	S
Dioxane	S	S	S	S	S	S	S	S
Ethanol (95%)	S	S	I	I	I	I	I	I
Ethyl Acetate	S	S	I	SW	S	S	S	S
Ethylene Dichloride	S	S	S	S	S	S	S	S
Ethylene Glycol	I	I	I	I	I	I	I	I
Ethyl Ether	S	S	I	I	I	I	I	I
Fenchone	S	S	I	G	S	S	S	S
Isophorone	S	S	S	S	S	S	S	S
Isopropanol (anhydrous)	I	PS	I	I	I	I	I	I
Isopropanol (technical)	S	S	I	I	I	I	I	I
Isopropyl Acetate (98%)	S	S	SW	SW	S	S	S	S
Mesityl Oxide	S	S	S	S	S	S	S	S
Methanol	S	S	I	I	I	I	I	I
Methyl <i>n</i> -Amyl Ketone	S	S	S	S	S	S	S	S
Methyl "Cellosolve"	S	S	I	I	S	S	S	S
Methyl "Cellosolve" Acetate	S	S	SW	SW	S	S	S	S
Methyl Isobutyl ketone	S	S	S	S	S	S	S	S
2-Nitropropane	S	S	PS	S	S	S	S	S
Petroleum Naphtha	I	I	I	I	I	I	I	I
Propylene Dichloride	S	S	PS	S	S	S	S	S
Propylene Oxide	S	S	PS	PS	S	S	S	S
Toluene	S	S	I	PS	SW	S	PS	S
Tricresyl Phosphate ⁽⁴⁾	I	I	S-CL	S	I	PS	I	S
Xylene	SW	PS	I	I	SO	PS	SW	PS

S = Soluble SO = Softens G = Gels CL = Cloudy Solution I = Insoluble
SW = Swells P = Partially

⁽¹⁾ Liquids in which the resins are soluble are not necessarily sufficiently active solvents to permit their use in "Vinylite" resin coating formulations.

⁽²⁾ Tests were made at temperatures slightly below the boiling points on those chemicals which boil below 95°.

⁽³⁾ These liquids are plasticizers which may be compatible with but are not necessarily solvents for the resins.

⁽⁴⁾ "Vinylite" resin AYAF, 10% in solvent.

⁽⁵⁾ "Vinylite" resin QYNA, 2% in solvent.

⁽⁶⁾ "Vinylite" resin VYHH, 10% in solvent.

⁽⁷⁾ "Vinylite" resin VYLF, 10% in solvent.

* Bakelite Corporation. Adapted.

Commercially useful vinyl chloride-acetate copolymers contain eighty-five per cent or more of vinyl chloride. Because of the preponderance of vinyl chloride in their structure, all of them are markedly different in physical properties from polyvinyl acetate. On the other hand, they do resemble polyvinyl chloride, the distinction here being one of degree rather than kind. Hence, although from a strictly chemical viewpoint, polyvinyl chloride can be classified apart from vinyl copolymers, from a practical angle the former should be considered as the limiting member of the family of commercial vinyl chloride resins, and it will be so dealt with in this text. On the basis of physical properties and practical applications, a more meaningful line of demarcation can be established between soft and hard vinyl chloride polymers and copolymers. Hard resins contain 95 per cent, or more, of vinyl chloride. Soft ones contain 92 per cent or less.

The hard resins are utilized in highly plasticized form for flexible and elastomeric products which are fabricated by extruding, calendering, molding, or solution-casting. No rigid moldings are made from them. In general, they are not employed for solution coatings, exceptions being the "Organosols" and "Plastisols," as well as certain coated fabrics. Like polyvinyl chloride itself, all of the hard vinyl chloride resins possess very restricted solubility in organic solvents and are dissolved appreciably only by nitrobenzene and cyclic ketones.

Soft vinyl chloride resins are utilized in unplasticized rigid moldings and rigid sheets, in textile fibers, and monofilaments, and in solution coatings. Although used to some extent, also, in certain plasticized goods, they are definitely inferior to their hard analogs with respect to flex-fatigue life. Soft resins are soluble in a wider range of ketones than their hard counterparts.

During recent years, the trend in volume production of vinyl resins has been toward polymers of high vinyl chloride content and high molecular weight.

General Properties of Vinyl Chloride Resins

In the unplasticized state, vinyl chloride polymers and copolymers possess specific gravities within the range of 1.35 to 1.40 at room temperature. Density increases slightly with vinyl chloride content. These resins are all thermoplastic. The hard members of the family possess relatively high softening points which are lowered with increasing vinyl acetate content. Vinyl chloride resins decompose before melting, with liberation of hydrogen chloride accompanied by discoloration. This fact makes it necessary to stabilize them thermally in order to convert them into useful articles. This subject is discussed in the next section.

Vinyl chloride resins in general possess excellent chemical resistance. They are unattacked by acids and alkalis at temperatures up to about 70°. They are not dissolved by either mineral or fatty oils, and, as shown by Table 43, they are insoluble in most solvents. Nitrobenzene and certain unsaturated and cyclic ketones such as mesityl oxide, isophorone, and cyclohexanone dissolve from 6 to 15 per cent, by weight, of polyvinyl chloride, while the lower aliphatic ketones take up less than two per cent. Soft vinyl chloride resins, while still possessing unusually good general chemical resistance, are more soluble in ketones than the hard polymers. Indeed, they dissolve so well in such aliphatic ketones as acetone, methyl ethyl ketone, and methyl isobutyl ketone that these liquids serve as solvents in the formulation of vinyl copolymer lacquers which can be thinned with considerable volumes of diluents like toluene.

Vinyl chloride resins are non-flammable, odorless, tasteless, and non-toxic. They are free from oxidation and therefore weather well upon both internal and external exposure. They resist the action of concentrated oxidizing acids and other severely corrosive chemicals such as chromium plating baths, gaseous chlorine, ozone, and sulfur chloride. Vinyl chloride resins are exceptionally water-resistant, unplasticized polymers often dissolving less than 0.05 per cent by weight after prolonged immersion at room temperature; this characteristic improves with increasing vinyl chloride content.

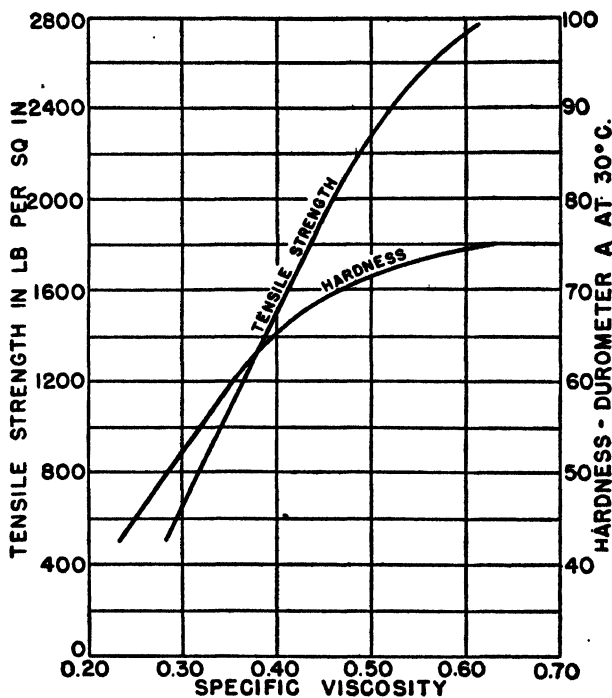
Vinyl chloride resins possess relatively high tensile strength. This and certain other physical properties such as hardness and flex-fatigue life improve with increasing molecular weight, as illustrated in Figure 121 (see page 320).

As in the case of most other plastics, tensile strength increases while elongation decreases with decreasing temperature. The relationship between the stress-strain properties of plasticized polyvinyl chloride and temperature is shown in Figure 122.

Rigid sheets and moldings of unplasticized soft resins are exceptionally resistant to warpage. In the case of elastomeric products made from plasticized hard resins, dimensional stability is contingent upon the nature of the plasticizer, as well as its amount, and by the conditions to which it is subjected. Like dimensional stability, other properties of the hard resins, including their mechanical, electrical, and chemical behavior, are also contingent upon the kind and quantity of plasticizer combined therewith, and upon the extent of pigmentation, if any.

Hard Vinyl Chloride Resins. It has been pointed out that almost all of the practical applications of the hard vinyl chloride resins require their plasticization and that the characteristics of the products vary with the kind and quantity of plasticizer used. Other classes of compounding

ingredients which are incorporated with hard resins include stabilizers against thermal decomposition, fillers, coloring materials, and mold lubricants. Stabilizers are always used; plasticizers almost always. Fillers may or may not be employed. Coloring materials, while frequently utilized in amounts ranging from 1 to 2 per cent, do not appear to exercise any influence upon physical properties. Lubricants are em-



Courtesy The B. F. Goodrich Co.⁸⁴

Figure 121. Relation between apparent specific viscosity of polyvinyl chloride and tensile strength and hardness of its plasticized compositions. (Specific viscosities of the polymer itself determined in an Ostwald pipette of 0.8 mm. bore using a 0.4 per cent solution of polymer in nitrobenzene at 20°. Tensile strength and hardness measured on compositions prepared by incorporating the various polymers in the basic recipe of 100 parts by volume of polyvinyl chloride to 75 parts of tricresyl phosphate.)

ployed where hard resins are to be extruded or molded, in order to prevent sticking to the metal surfaces of the tuber or other equipment. From 1 to 3 per cent of the formula weight is generally employed, the most useful materials being carnauba wax, stearates, and mineral oil. The latter is especially satisfactory in wire coating operations. Except for

metal stearates, lubricants do not appear to influence other physical properties of the compounds. Metal stearates may act as thermal stabilizers also.

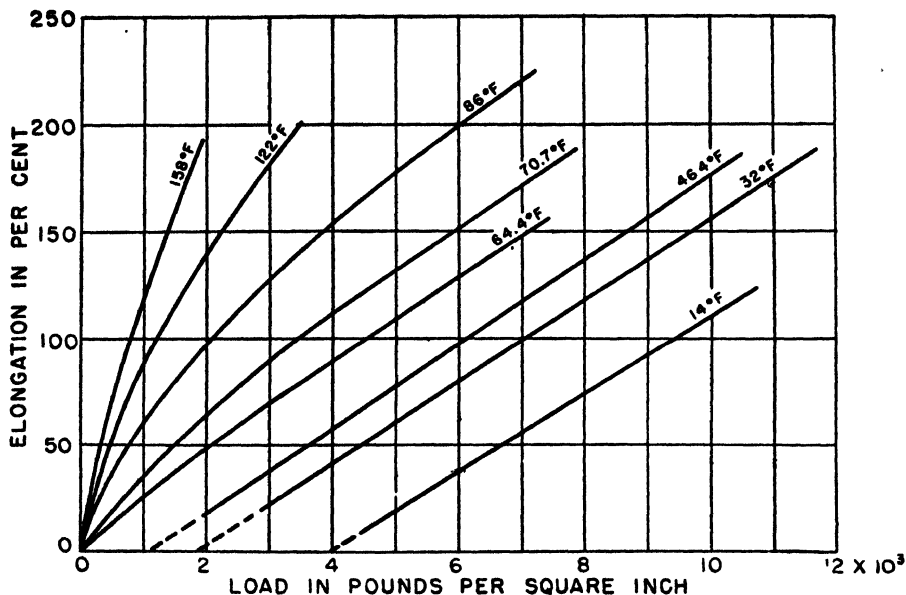


Figure 122. Stress-strain diagrams for 60:40 polyvinyl chloride-tricresyl phosphate compositions at various temperatures. (Russell⁸²)

Thermal Stabilization

Like most chlorinated high polymers, vinyl chloride resins exhibit a tendency to decompose on long standing in the light under atmospheric conditions or on long-continued moderate heating. Decomposition becomes apparent at temperatures above about 300° F. While most physical properties are scarcely affected as a result of thermal instability, color does develop. The resins yellow at first, then become darker, and finally blacken if heating is sufficiently intense. Decomposition is accompanied with evolution of traces of hydrogen chloride which catalyzes further decomposition, the reaction being autocatalytic. For this reason, thick films from which acid cannot readily escape exhibit greater thermal instability than thin ones.

Iron and zinc surfaces and pigments accelerate decomposition. Special care should therefore be exercised in using these materials in conjunction with vinyl chloride resins at elevated temperatures, although a large number of vinyl raincoats have been made with the use of iron oxide pigments and have given satisfactory military service.

Several different categories of chemical compounds are effective stabilizers. Many basic substances are utilized commercially and probably act by virtue of their ability to combine with traces of free acid and remove it from the sphere of action. In other instances, however, there is some other as yet unknown explanation for the effectiveness of a given stabilizer. If the development of color is dependent upon the formation of a chromophore containing a conjugated system of double bonds resulting from dehydrohalogenation, it may be that certain stabilizers like maleic anhydride function by virtue of a Diels-Alder addition across the conjugated system, thus eliminating the chromophore.

Compounds which are used as stabilizers include calcium, cadmium and lead soaps, calcium and lead acetates, oxides of bismuth, barium and lead, silicates of sodium, calcium and lead, and lead salts of substituted phenols like *para*-tertiary butyl phenol. Among these materials, lead silicate, basic white lead, calcium stearate, and lead stearate are especially useful where clarity or non-toxicity are unimportant. From two to five per cent of these stabilizers, based on the total formula weight, is employed. In Germany, phenyl indol was used as a stabilizer. Numerous other compounds have been patented for this purpose. The most effective inhibitors of thermal decomposition appear to be organo-metallic compounds containing tin or lead. Dibutyl tin laurate is especially valuable and is used in amounts up to 2 per cent by weight of resin to maintain water-white clarity in transparent vinyl copolymers. Addition of maleic anhydride to copolymer resins containing organo tin salts still further improves stability; the equivalent effect can be obtained by use of dibutyl tin maleate or a similar organo tin salt of an alpha-unsaturated acid. Excellent color stabilization can be brought about by combination of two or more inhibitors as, for example, 1 per cent by weight of calcium ethyl acetoacetate and 0.05 per cent of dibutyl tin maleate.

Plasticization

Hard vinyl chloride resins almost always require plasticization to convert them into useful materials. Where suitably formulated, they acquire elastomeric characteristics. Many plasticizers can be incorporated under heat and pressure, by means of hot rubber rolls. It has already been noted that copolymers, even where the acetate is present to less than 0.5 per cent, are easier to handle on the mill than polyvinyl chloride itself.

The plasticizers most commonly used with hard vinyl chloride resins, listed in the order of their importance, are as follows:

di-2-ethylhexyl phthalate ("Flexol" DOP) (often called dioctyl phthalate)

tricresyl phosphate ("Kronitex AA," "Lindol")

dicapryl phthalate

butyl esters of acetylated polymerized ricinoleic acids ("P-16")

dibutoxyethyl phthalate ("Kronisol")

tri-2-ethylhexyl phosphate (often called trioctyl phosphate)

methoxyethyl acetyl ricinoleate ("KP-120," "P-4C")

triethylene glycol di-2-ethylhexoate ("Flexol" 3GO)

triethylene glycol esters of coconut oil fatty acids ("SC" plasticizer)

The effect of these materials upon hard vinyl chloride resins can be judged from Table 44.

Di-2-ethylhexyl phthalate is commonly used for general purpose plasticization. Methoxyethyl acetyl ricinoleate yields films possessing relatively little temperature sensitivity. Triethylene glycol di-2-ethylhexoate ("Flexol" 3GO) (like polyethylene glycol di-2-ethylhexoate, "Flexol" 4GO) is especially well suited for low temperature flexibility. Numerous other plasticizers are less frequently used such as butyl phthalyl butyl glycolate ("Santicizer B-16"), dibutyl phthalate, diamyl phthalate, dibutyl sebacate, di-2-ethylhexyl sebacate, and tributyl phosphate.

Plasticizers for hard vinyl chloride resins are generally employed in amounts ranging from 25 to 45 per cent of the total formula weight. At times, it is desirable to combine two or more plasticizers, such as di-2-ethylhexyl phthalate and tricresyl phosphate.

While elongation and flexibility are greatly increased by plasticization, both tensile strength and hardness are diminished almost in proportion to the amount of plasticizer. This fact is illustrated in Figure 123.

The plasticizers which are used in conjunction with hard vinyl chloride resins are much more soluble in most organic solvents than the resins themselves, although there does not appear to be any direct relation between solubility of a given plasticizer in oil and its extraction thereby. Loss of plasticizer from hard copolymer resin films immersed in mineral oil for ten days is listed in Table 44. Figure 124 illustrates the loss in weight of plasticized polyvinyl chloride upon immersion in mineral oil, although in this case the tensile strength is not altered.

Immersion of plasticized hard resins in potent solvents may lead to serious plasticizer extraction, attended by deterioration of physical properties.

Although the vinyl chloride resins themselves possess an exceptional degree of dimensional stability, plasticization induces some cold flow and creep, especially at elevated temperatures. Elastomeric compositions based on hard resins, therefore, may acquire a permanent set which increases with both temperature and plasticizer content, as shown in Figure 125.

The effect of plasticization on flexibility, brittle point, abrasion re-

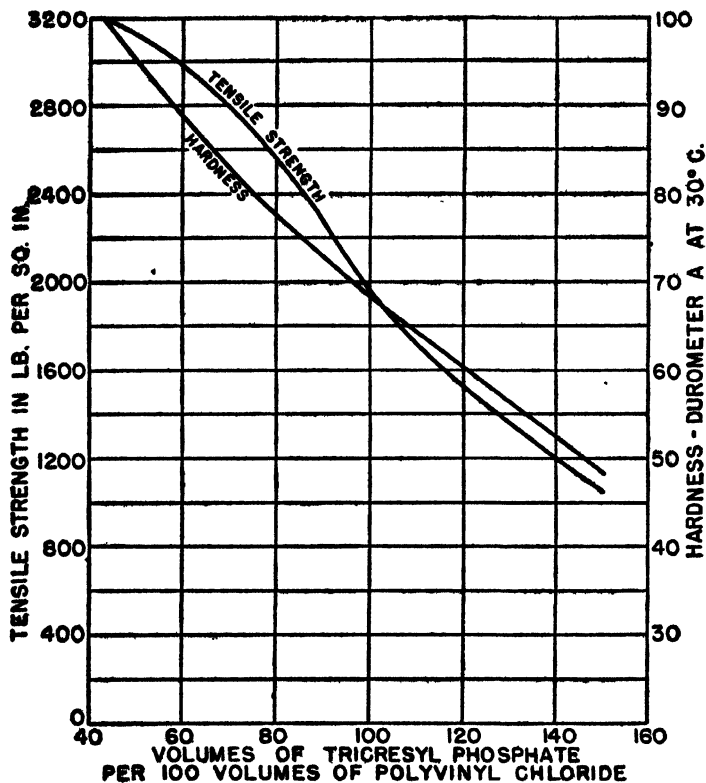
Table 44. Properties of "Vynlite" VYNW Compounds with Varying Amounts of Nine Important Plasticizers^a

No.	Plasticizer	% by Weight*	10°	% Elongation 25°	40°	% Lost in 10 Days from 0.004 Inch Film			Heat Stability Hr. at 160°	Flex Temp. (°C)	Sweat-Out
						Air, 60°	Water, 25°	Oil, 25°			
1	Di-2-ethylhexyl phthalate	30	29	70	149	0.7	0.3	5.3	8.0	-10.5	No
		35	57	115	208	0.8	0.2	10.0	10.0	-19.5	No
		40	100	175	288	1.4	0.2	16.5	10.0	-34.5	No
		33.5	47	100	187	0.7	0.3	8.2	9.5	-16.0	No
2	Tricresyl phosphate	30	10	45	148	0.2	0.1	0.4	1.5	+13.0	No
		35	19	95	211	0.5	0.9	1.4	1.5	+5.0	No
		40	49	156	320	0.6	2.1	4.2	1.5	-6.0	No
		35.3	20	100	218	0.5	1.0	1.5	1.5	+4.2	No
3	Dicapryl phthalate	30	20	54	116	1.0	0.1	6.9	8.0	-7.5	No
		35	50	95	181	1.4	0.2	15.4	7.0	-21.0	No
		40	81	150	249	1.1	0.4	27.9	7.5	-31.0	No
		35.6	53	100	189	1.2	0.2	16.9	7.5	-22.0	No
4	Butyl ester of acetylated polymerized ricinoleic acids	30	25	63	128	6.0	3.4	13.0	1.0	-31.5	Yes
		35	60	101	168	11.3	4.7	16.2	1.0	-34.5	Yes
		40	98	155	231	10.2	5.5	22.2	1.0	-44.0	Yes
		34.8	58	100	166	10.9	4.6	16.1	1.0	-34.0	Yes
5	Dibutoxyethyl phthalate	30	32	90	171	2.1	4.8	7.3	5.0	-12.7	No
		35	68	135	258	2.0	4.9	14.7	3.0	-22.1	No
		40	117	210	338	5.2	18.5	11.4	2.0	-33.4	No
		31.3	42	100	193	2.1	4.8	11.4	4.5	-15.0	No
6	Tri-2-ethylhexyl phosphate	30	38	80	152	1.9	0.3	16.3	3.0	-41.0	No
		35	70	128	208	2.5	0.4	23.0	3.0	-55.0	No
		40	124	189	271	3.6	0.4	29.3	3.0	-62.0	No
		32.3	50	100	178	2.2	0.3	19.5	3.0	-49.5	No

7	Methoxyethyl acetyl ricinoleate	30	40	81	151	2.8	0.8	11.5	1.5	- 23.0	No
		35	69	120	198	2.2	1.6	16.9	1.5	- 37.0	No
		40	109	178	290	2.2	2.2	22.3	1.5	- 49.5	No
		32.6	54	100	172	2.4	1.3	14.5	1.5	- 30.5	No
8	Triethylene glycol di-2-ethyl hexoate	30	48	88	159	8.4	2.0	15.3	4.0	- 31.5	No
		35	81	135	225	10.1	2.6	21.2	5.0	- 44.5	No
		40	118	175	289	6.2	2.7	26.4	5.0	- 58.0	Yes
		31.2	55	100	175	8.4	2.0	17.2	4.5	- 34.5	No
9	Triethylene glycol esters of coconut oil acids	30	72	117	188	5.1	8.8	20.0	5.0	- 39.0	Yes
		35	96	153	251	4.7	9.1	25.0	5.0	- 52.0	Yes
		40	143	209	310	4.8	11.4	30.0	5.0	- 62.5	Yes
		29.3	54	100	177	4.1	8.2	20.0	5.0	- 36.0	Yes

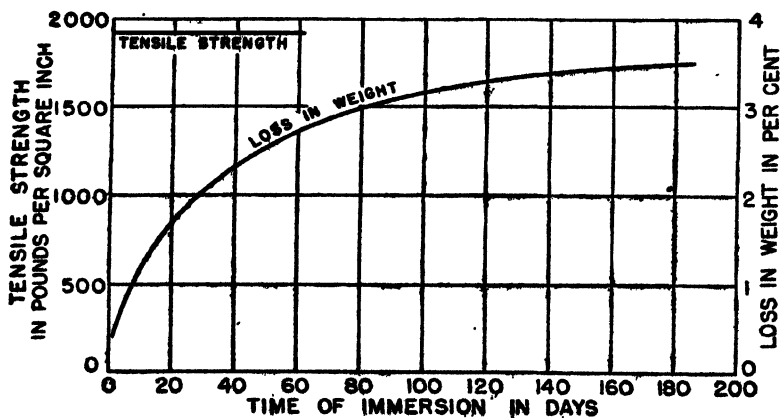
* Formulas of compounds in per cent by weight:

Resin	66.97	62.21	57.42
Lubricant	1.01	0.93	0.86
Stabilizer	2.02	1.86	1.72
Plasticizer	30.00	35.00	40.00
	100.00	100.00	100.00



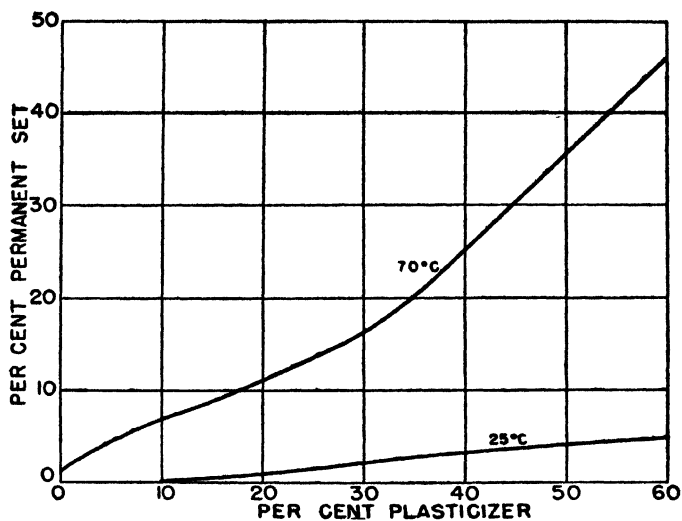
Courtesy The B. F. Goodrich Co.⁵⁴

Figure 123. Relation between plasticization of polyvinyl chloride, tensile strength, and hardness.



Courtesy The B. F. Goodrich Co.⁵³

Figure 124. Change in weight and in tensile strength of "Koroseal" caused by immersion in paraffinic oils.



Courtesy The B. F. Goodrich Co.⁵⁸

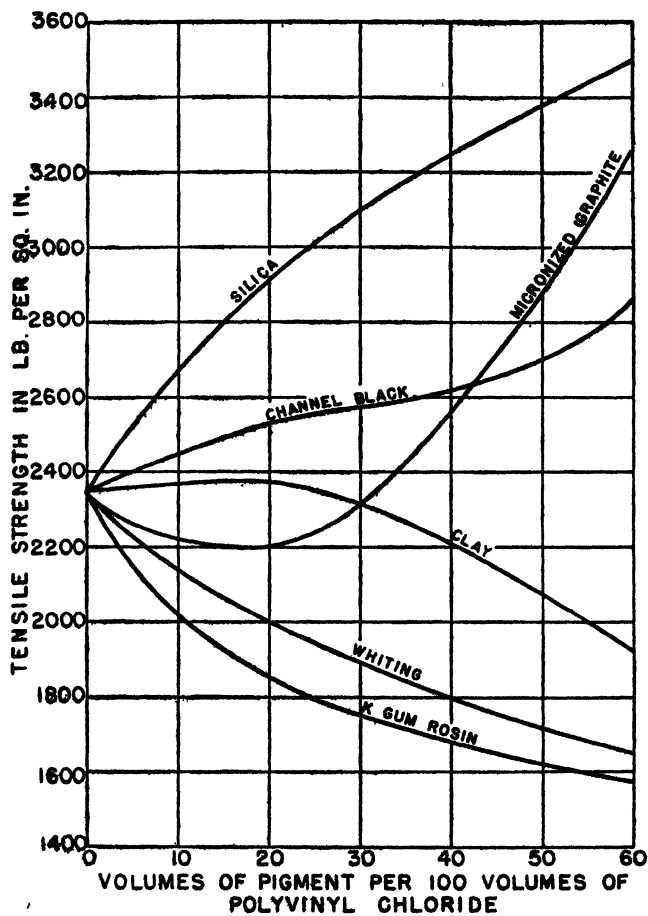
Figure 125. Relation between permanent set and plasticizer content of "Koroseal" (plasticized polyvinyl chloride) at two different temperatures. Samples one inch square by 3/32 inch thick were placed between smooth, flat, steel plates and loaded to 400 lbs per square inch and exposed to 158° F for 22 hours in an oven. Ten minutes after removal, the decrease in thickness was measured on a Randall-Stickney gauge. The permanent set is expressed as per cent decrease of original thickness. Tests were repeated at room temperature (average 70° F). A rubber compound particularly designed for low set characteristic in compressive service showed 4.17 per cent set at the elevated temperature and 1.04 per cent set at room temperature.



Courtesy Bakelite Corp.

Figure 126. Milling "Vinylite" plastic compounds.

sistance, and dielectric properties is discussed in connection with specific applications of hard resins. In general, toughness and dielectric properties improve as the amount of plasticizer is decreased, but flexibility—especially at low temperatures—suffers accordingly..



Courtesy The B. F. Goodrich Co.⁵⁴

Figure 127. Relation between loading of polyvinyl chloride and ultimate tensile strength. (Basic recipe: 100 parts polyvinyl chloride to 89 parts tricresyl phosphate.)

Loading

Plasticized hard vinyl chloride resins can be milled together with other compounding ingredients, such as fillers. Common fillers used for this purpose include the carbon blacks (best medium soft), fine clays, silica, diatomaceous earth, barytes, and soft whiting. Most of these materials

exercise little, if any, reinforcing action on the hard vinyl chloride resins, but they are sometimes utilized in compounding vinyl elastomers for mechanical applications where special control of hardness or some other specific property is sought. Certain relationships between filler content and physical properties of plasticized polyvinyl chloride are shown in Figures 127 to 130.

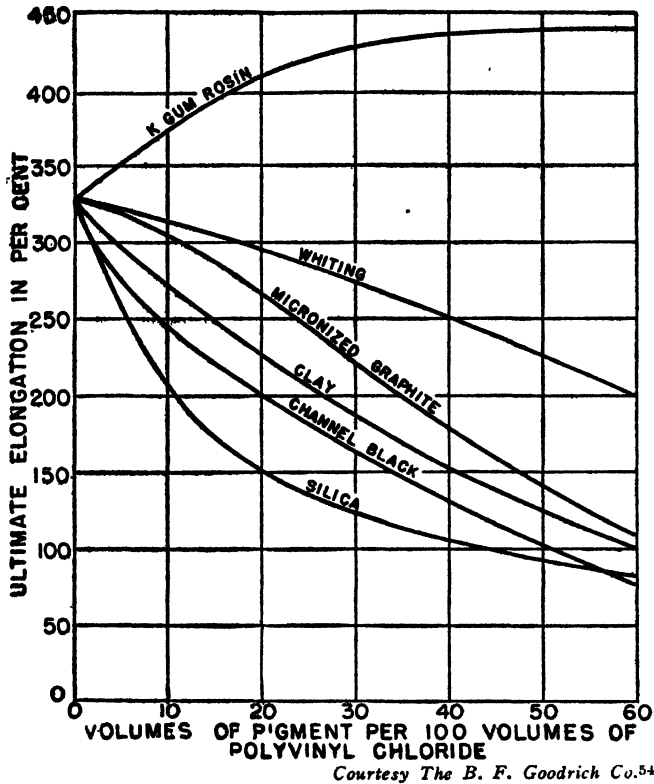


Figure 128. Relation between loading of polyvinyl chloride and elongation at the breaking point. (Basic recipe: 100 parts polyvinyl chloride to 89 parts tricresyl phosphate.)

The effect of loading on dielectric properties and abrasion resistance is discussed under specific applications of hard vinyl resins. It is usually harmful in both cases.

Uses of Hard Vinyl Resins

Wire and Cable Coating: Extruded Products. The most important use of hard vinyl chloride resins is in electric wire and cable coating. This single application has accounted in large part for the spectacular growth

of vinyl resin production since Pearl Harbor. Their utility for this application is based upon good electrical properties, flexibility where properly plasticized, good aging characteristics, ability to withstand chemical and

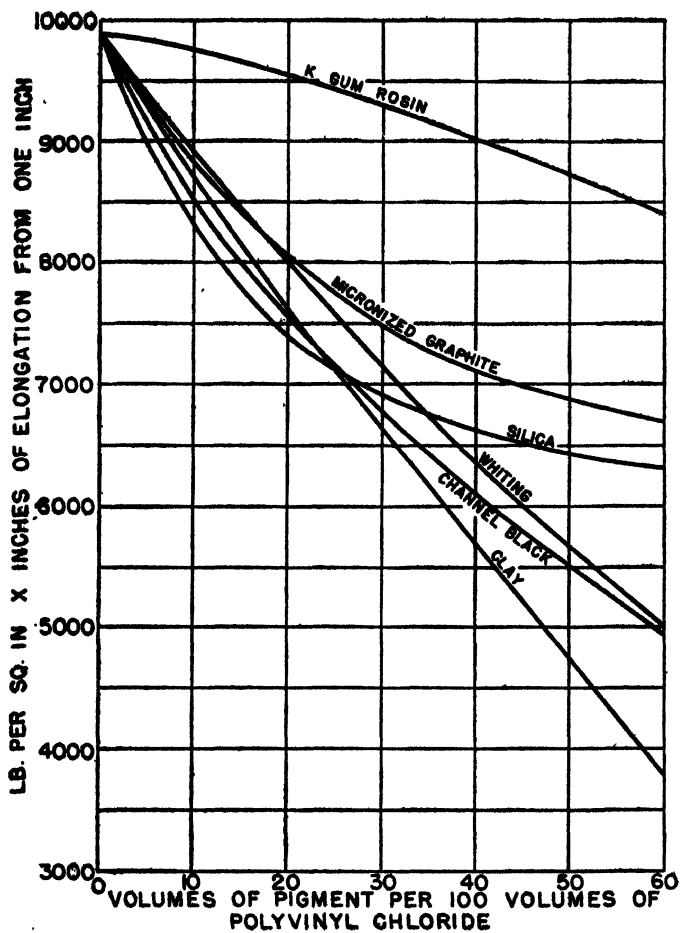
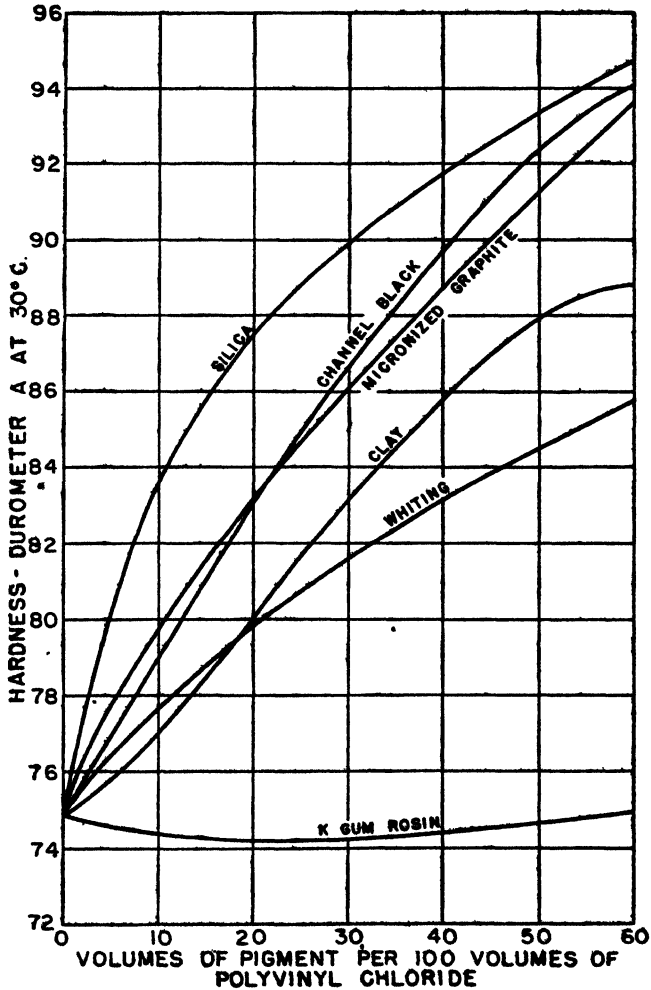


Figure 129. Empirical combined effect on tensile strength and elongation of loading of polyvinyl chloride. (Basic recipe: 100 parts polyvinyl chloride to 80 parts tricresyl phosphate.)

mechanical abuse, and non-flammability. These resins are extruded for wire and cable coating either directly or in the form of insulating tape. The latter has proved invaluable in automotive and aircraft lighting and ignition circuits, as well as in industrial and naval cables. Wrapped tape insulation can be heat-sealed at temperatures between 90 and 150° to

yield excellent electrical and mechanical protection which is impervious to moisture.

In compounding hard vinyl resins for wire and cable coating, the resin



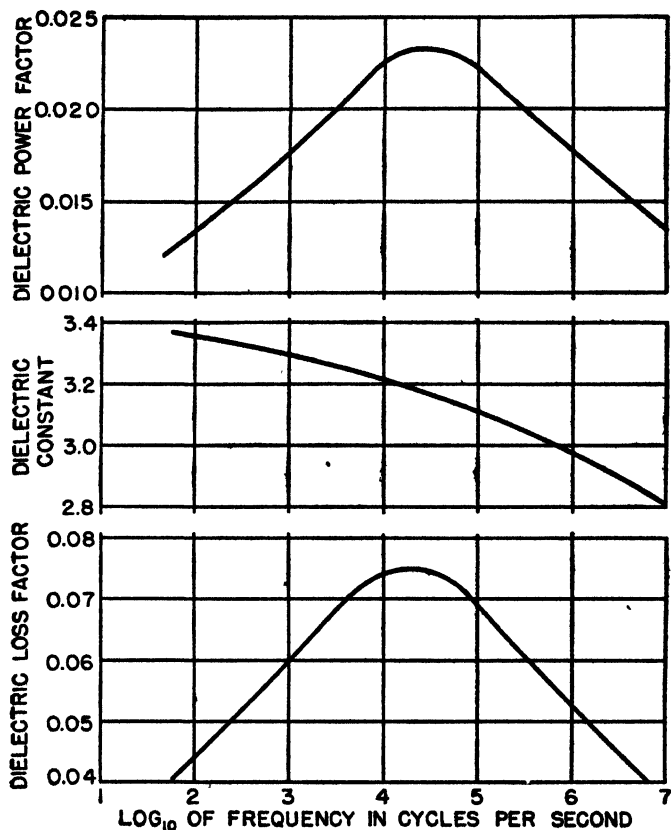
Courtesy The B. F. Goodrich Co.⁵⁴

Figure 130. Relation between loading of polyvinyl chloride and hardness. (Basic recipe: 100 parts polyvinyl chloride to 89 parts tricresyl phosphate.)

is admixed with plasticizer, stabilizer, lubricant, and filler if present, and cold-mixed in a standard chromium-plated or stainless steel kneader or mixer for about a half-hour. After discharging into drums, it is allowed to stand for several hours, preferably a day, and then fluxed and milled

for about 15 minutes on rubber rolls having a speed differential of about 1.2/1 and heated to 135–149°.

The dielectric properties of all plasticizers used in conjunction with vinyl resins are inferior to those of the resins themselves, so that in order to obtain flexibility by plasticization, some sacrifice of insulating value



Courtesy Halowax Products Division of U. C. C.⁵⁵

Figure 131. Dielectric properties of "Vinylite" VYNW material at 25°. (Formula: 96 per cent "Vinylite" VYNW; 1 per cent lead stearate; 2 per cent white lead; 1 per cent mineral oil.)

must be made. The dielectric characteristics of a hard copolymer resin containing no plasticizer are shown in Figure 131. Figures 132 and 133 show the effect of adding various amounts of two of the most important plasticizers. Figure 134 shows the relation between d.c. resistivity, temperature, and plasticizer content.

The nature of the plasticizer also exercises an influence on the aging properties of compounded hard resins as shown in Figure 135.

In general, the loading of extrusion compounds with large volumes of fillers results in deterioration of dielectric properties and should be avoided, especially where the wire or cable coating must possess good voltage breakdown and insulation resistance after prolonged immersion

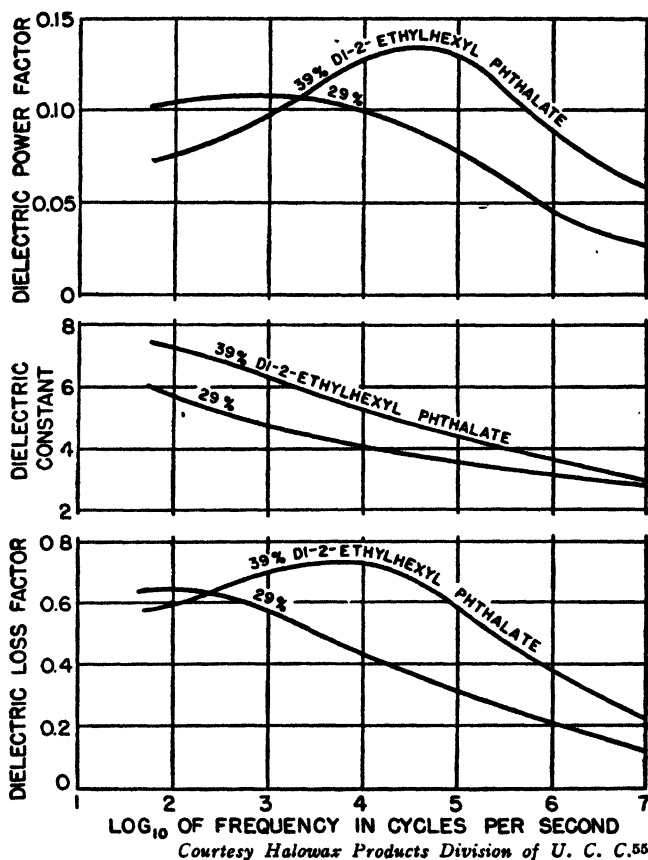


Figure 132. Effect of plasticizer content on the dielectric properties of "Vinylite" VYNW—di-2-ethylhexyl phthalate compounds at 23°. (4-inch disc specimens. Formula: calcium stearate, 1 per cent; di-2-ethylhexyl phthalate, as indicated; "Vinylite" VYNW, balance to 100 per cent.)

in water. Where the latter requirement does not exist, filling with only a minor amount of filler may, in some instances, result in improved resistivity, although it is reduced by further loading, as shown by Figure 136.

In addition to wire and cable coating, plasticized hard vinyl chloride resins are used in other extruded forms, especially as tubing for a variety

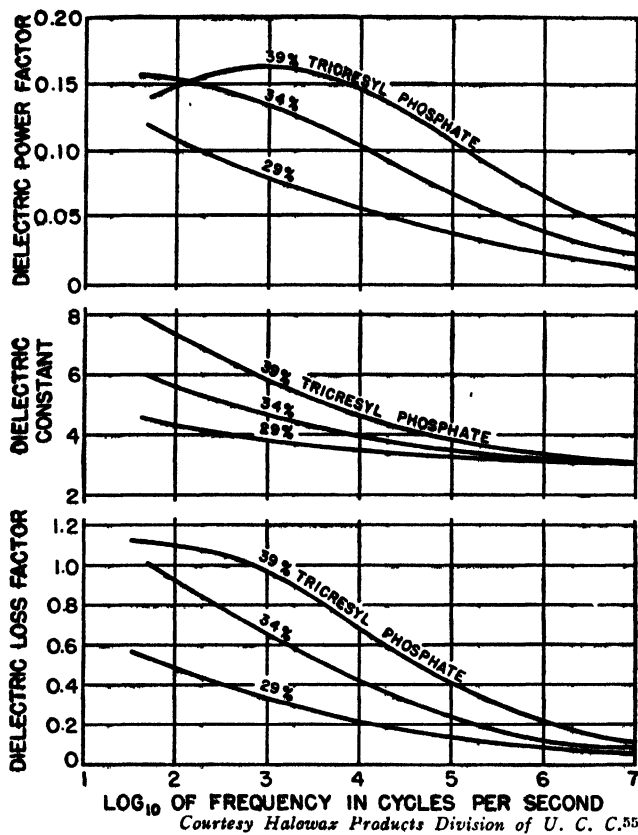
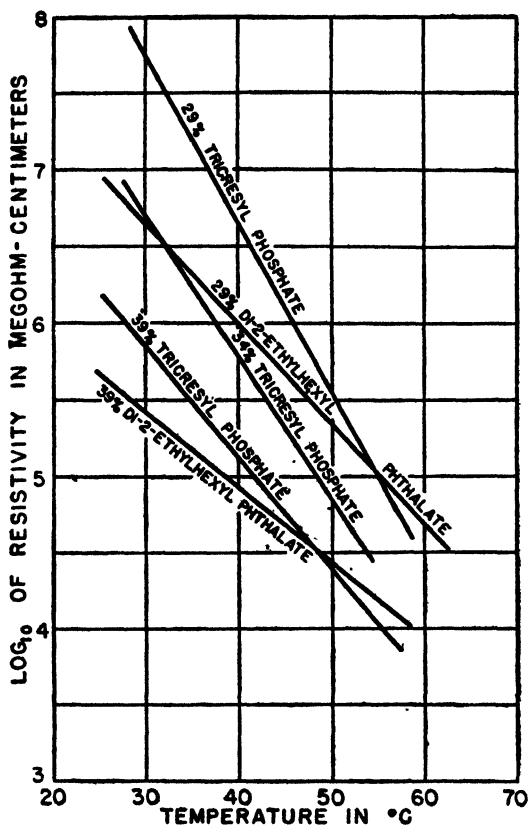


Figure 133. Effect of plasticizer content on the dielectric properties of "Vinylite" VYNW—tricresyl phosphate compounds at 23°. (4-inch disc specimens. Formula: calcium stearate, 1 per cent; tricresyl phosphate, as indicated; "Vinylite" VYNW, balance to 100 per cent.)



Courtesy Halowax Products Division of U. C. C.⁵⁵

Figure 134. D. C. resistivity-temperature characteristics of 4-inch disc specimens of experimental "Vinylite" VYNW extrusion compounds. (Formula: calcium stearate, 1 per cent; plasticizer, as indicated; "Vinylite" VYNW, balance to 100 per cent.)

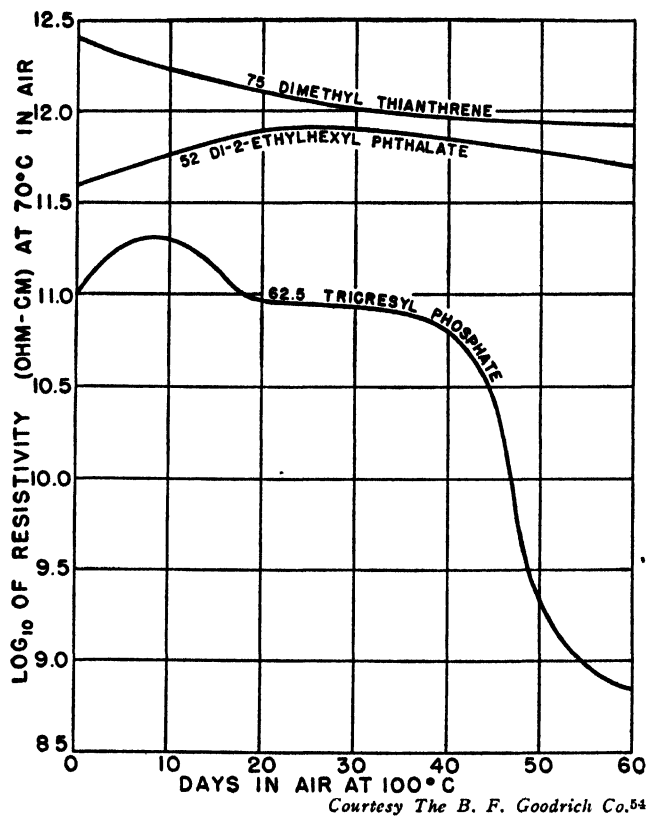
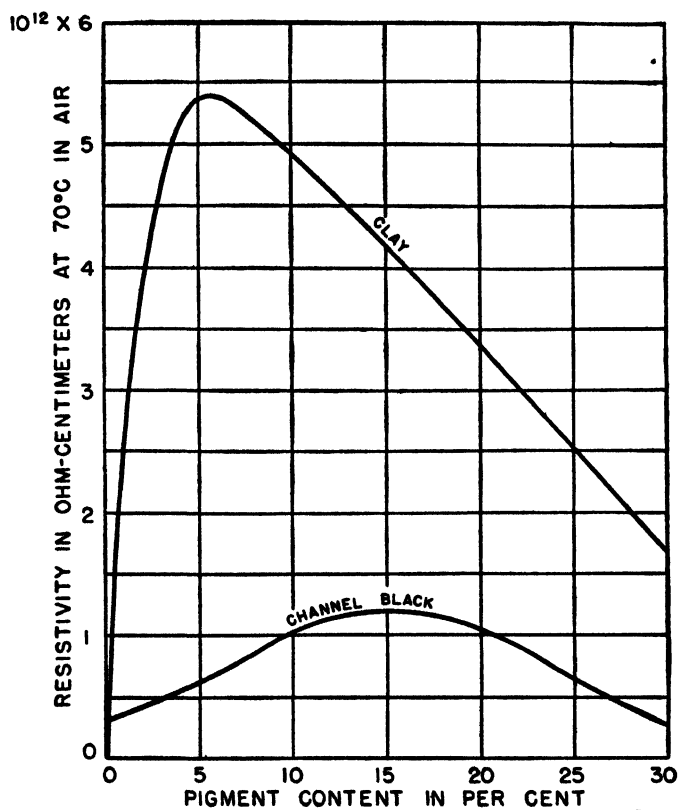


Figure 135. Effect of aging on electrical resistivity of polyvinyl chloride plasticized with optimum volumes of three plasticizers.



Courtesy The B. F. Goodrich Co.⁵⁴

Figure 136. Effect of varying amounts of certain fillers on electrical resistivity of plasticized polyvinyl chloride. (Formula: 100 per cent polyvinyl chloride, 52 per cent di-2-ethylhexyl phthalate, fillers as indicated based on 100 per cent resin.)

of purposes, including chemical equipment and beverage hose and as stripping for articles of attire such as belts, suspenders, and watch straps.

Flexible Sheeting and Film. Plasticized polyvinyl chloride in the form of molded sheets of varying thickness has been used in the field of mechanical goods, especially gaskets, for over a decade. The range of properties available in this material is indicated by Table 45.

Table 45. Physical Properties of Plasticized Polyvinyl Chloride ¹⁴

Specific gravity	1.20 to 1.41 (unpigmented)		
Specific volume	23.0 to 19.8 cubic inches per pound (unpigmented)		
Specific heat	0.32 to 0.51		
Coefficient of friction		<i>Bone hard</i>	<i>Soft</i>
	Dry	0.13-0.16	0.20-1.80
	Lubricated	0.13-0.16	0.05-0.10
Tensile strength	2000-3000 lb/sq in (batch stocks)		
Hardness (Shore durometer Type A at 30°)	60 to 100 (batch stocks)		
Elongation	2 to 500%		
Compression set	This varies considerably depending upon the exact compound, but is generally somewhat greater than rubber compounds.		
Volume compressibility	Practically incompressible.		
Tearing strength	Very tear-resistant — generally comparable with rubber compounds.		
Flexibility	Much better than rubber at normal temperatures in flexing life tests. Certain compounds will flex at temperatures as low as - 40°.		
Impact strength	100 inch pounds per sq in at room temperature. The softer compounds behave generally like rubber.		
Abrasion resistance	Koroseal is better than rubber at normal temperatures but softens and flows at elevated temperatures.		

Plasticized sheeting and film is produced from hard copolymer vinyl resins by calendering. Resistance to tearing, scuffing, and abrasion are outstanding attributes of these materials. A wide variety of colors—transparent, translucent, and opaque—is available. Sheeting is currently produced in thicknesses ranging from 0.020 inch to 0.085 inch. Film is available in thicknesses of 0.004 and 0.008 inches.

The rough surface finish imparted by calendering is most common, but sheeting may be press-polished or embossed. Surface-polished to simulate leather, vinyl sheeting has proved especially serviceable in toes and heels of boys' shoes where its scuff-resistance is outstanding. Other impressive applications have been made in wearing apparel and accessories such as belts, suspenders, ladies' evening shoes, and handbags, luggage, and upholstery. Heavier stock has been used in shoe soles. Film has proved popular in raincoats, shower curtains, drapes, food bags, and beauty parlor capes. It possesses intriguing potentialities as a food-

packaging material. Important military applications include jungle bags, aerial delivery bags, aircraft wing paulins, gun covers, hospital sheeting, desalination bags, and reconnaissance boat bladders.

In these uses, flexibility, lack of brittleness at low temperature, flex-

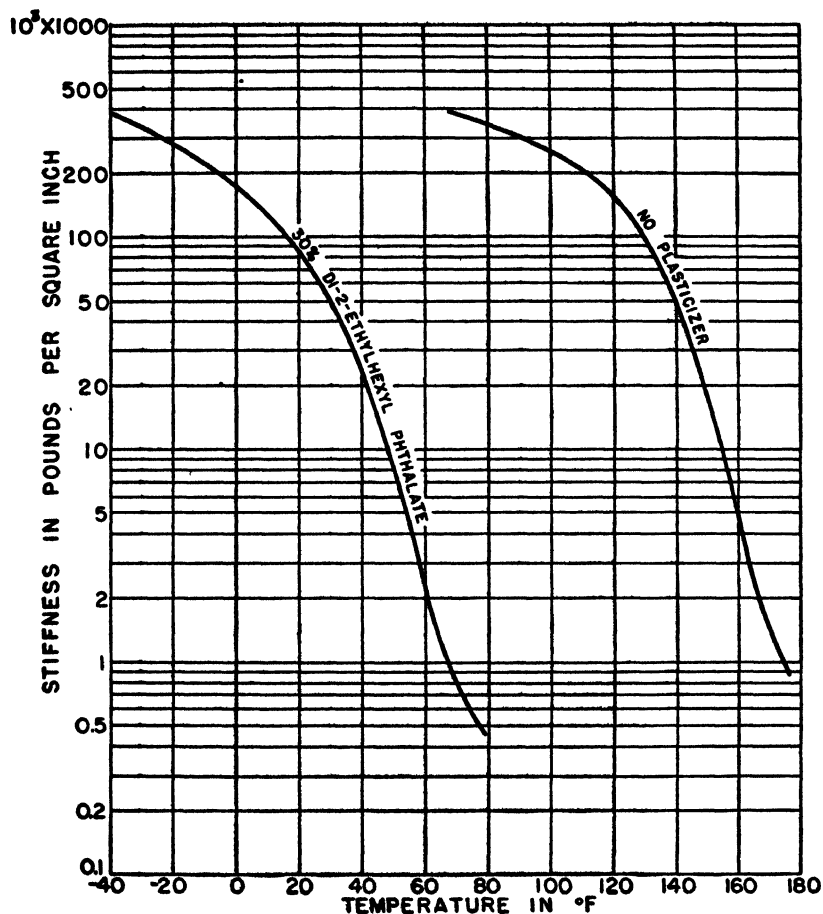


Figure 137. Stiffness versus temperature of unplasticized "Vinylite" VYNS compared with the same resin plasticized with 30 per cent di-2-ethylhexyl phthalate. (*Clash and Berg*³²)

fatigue resistance, and abrasion resistance are invaluable characteristics of properly plasticized hard vinyl chloride resins.

The extent to which plasticization improves stiffness-temperature relations of vinyl chloride resins in general is typified by the effect of incorporating di-2-ethylhexyl phthalate, to the extent of 30 per cent, with a soft copolymer, illustrated in Figure 137. The relation between plasti-

cizer content and stiffness of hard vinyl chloride copolymer resin sheeting at a given temperature is shown in Figure 138, where plasticization is carried out with di-2-ethylhexyl phthalate.

The effects of a given amount of different plasticizers and of varying

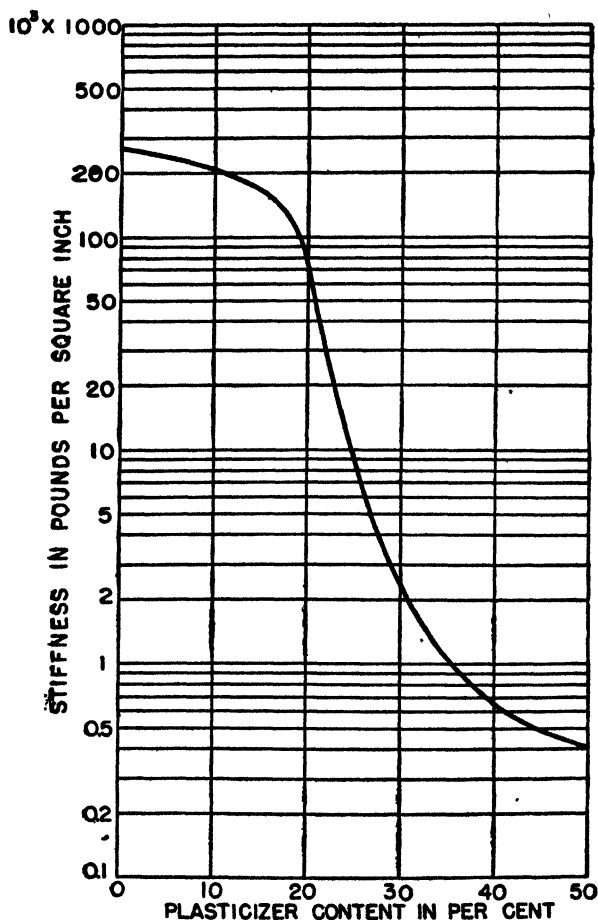


Figure 138. Stiffness at 25° of "Vinylite" VYNW plasticized with di-2-ethylhexyl phthalate vs. plasticizer content. (*Clash and Berg*³²)

amounts of the same plasticizer on stiffness-temperature relationships and brittle points of a hard copolymer resin are shown in Figures 139 and 140, respectively. Figure 141 shows the relation between brittle temperature and plasticizer content in the case of three important plasticizers.

Flex-fatigue life of plasticized vinyl chloride resin sheeting increases as a logarithmic function of the plasticizer content, as shown by Figure

142 which also illustrates the increasing longevity of these sheetings with rising temperature and the deleterious effect of stretching.

Unlike stiffness-temperature characteristics, flex-fatigue life is not a function of the type of plasticizer, but is determined almost entirely by

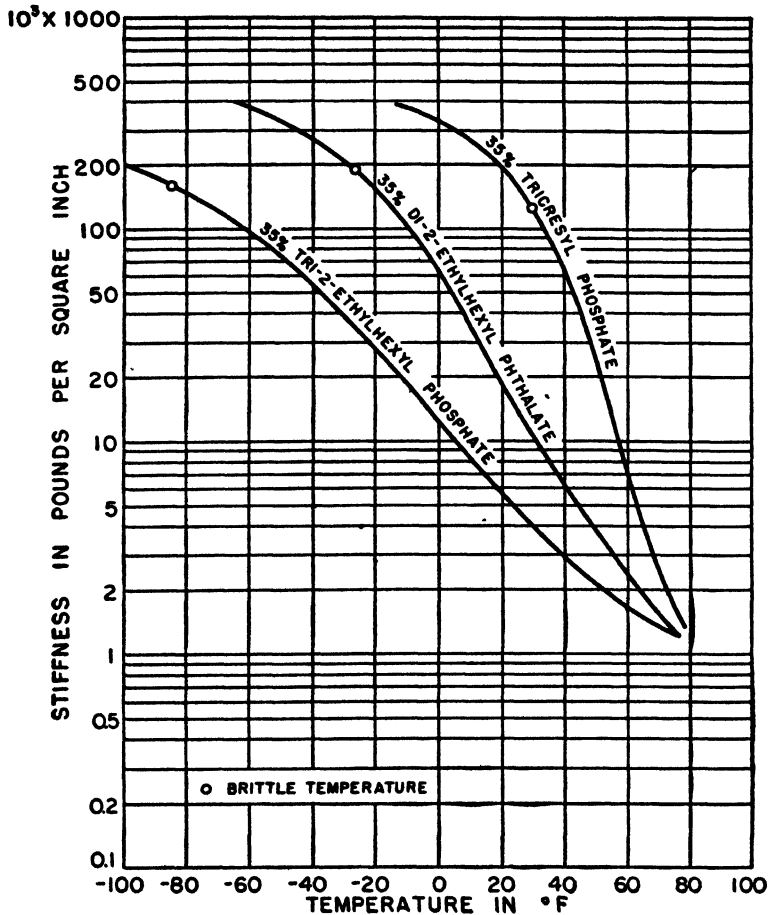


Figure 139. Stiffness vs. temperature of "Vinylite" VYNW plasticized with 35 per cent of three different plasticizers. (*Clash and Berg*³²)

the degree of flexibility of the compounded sheeting, regardless of the chemical nature of the plasticizer, provided it is readily compatible with the resin.

Other factors which affect the flex-fatigue life of vinyl sheeting include the molecular weight of the resin, the surface finish of the sheeting, and the presence or absence of fillers. In general, the higher the molecular

weight of the resin, the longer its fatigue life. Press-polished sheeting has two or three times the flex-fatigue life of material exhibiting sharp surface irregularities, such as a matte finish. Finally, the incorporation of fillers

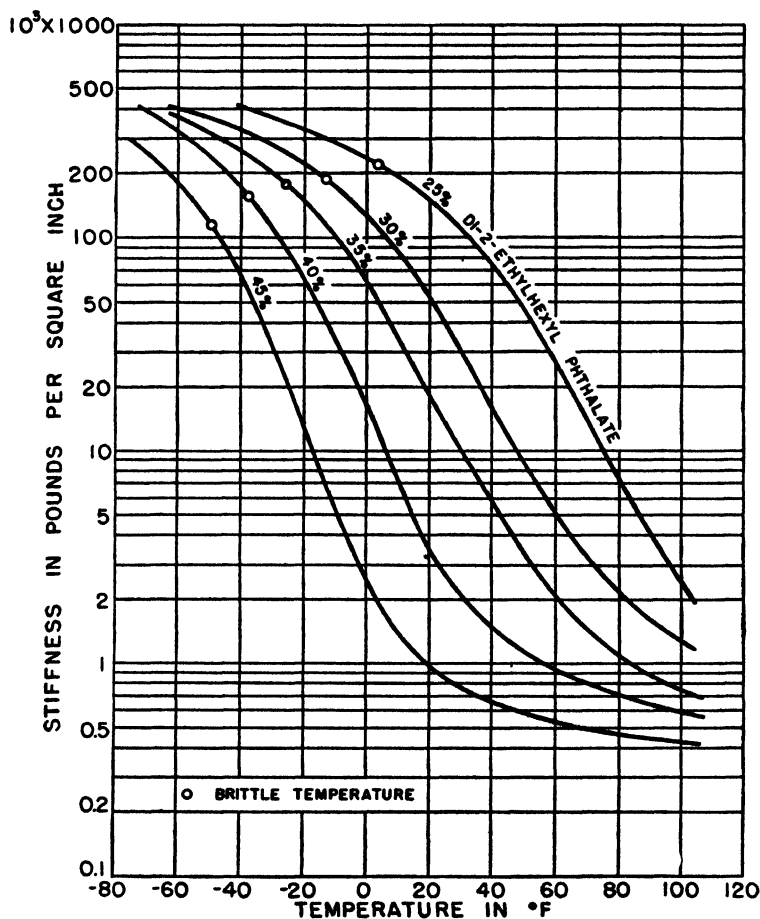


Figure 140. Stiffness vs. temperature of "Vinylite" VYNW plasticized with varying amounts of di-2-ethylhexyl phthalate. (*Clash and Berg*³²)

with plasticized hard vinyl chloride resins results in marked diminution of fatigue life, as shown by Figure 143.

Abrasion characteristics of plasticized vinyl sheeting are also highly important from such practical viewpoints as adaptability to shoe manufacture and upholstery construction. Curiously, the abrasion resistance of equally flexible sheeting is slightly more for plasticized soft resin of

medium molecular weight containing 90 per cent vinyl chloride than for high molecular weight hard resin. This fact is shown in Figure 144.

Abrasion loss of all types of vinyl resins decreases rapidly as the plasticizer content increases as illustrated by Figures 144 and 145. Like stiffness characteristics, but unlike flex-fatigue life, the resistance of plasticized vinyl resins to abrasion is influenced markedly by the chemical nature of the plasticizer (see Figure 145).

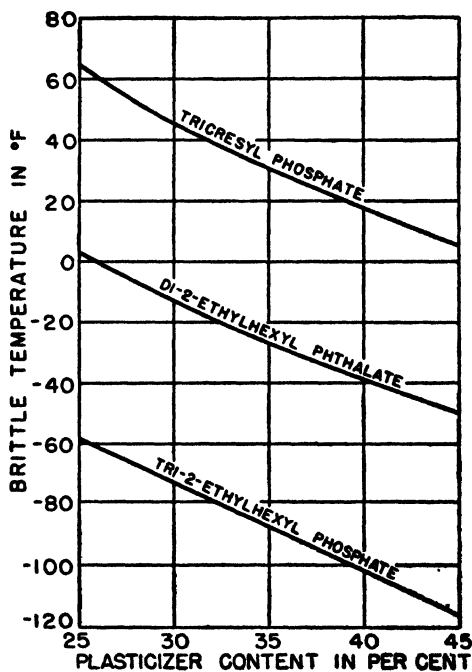


Figure 141. Effect of plasticizer concentration on brittle temperature of "Vinylite" VYNW. (ASTM Method D-746-43T.) (Clash and Berg³²)

It is of importance, also, to note that the abrasion resistance of plasticized vinyl chloride resin sheetings is very little affected by temperature changes within the range of 0 to 25°. This fact is again illustrated by Figure 144, which contrasts with these resins the marked temperature sensitivity of plasticized polyvinyl butyral sheeting. The latter material exhibits much higher abrasion loss at freezing than at room temperature. Rubber, on the other hand, shows less abrasion at 0° than at 25°.

Fillers greatly reduce abrasion resistance. The least degradation of abrasion properties occurs with the finest particles; the greatest, with the coarsest. The behavior of fillers in this respect is similar in all types of vinyl sheeting. These generalities are illustrated in Figures 146 and 147.

Although it is apparent from the foregoing discussion that the properties of sheeting and film made from plasticized hard vinyl chloride resins

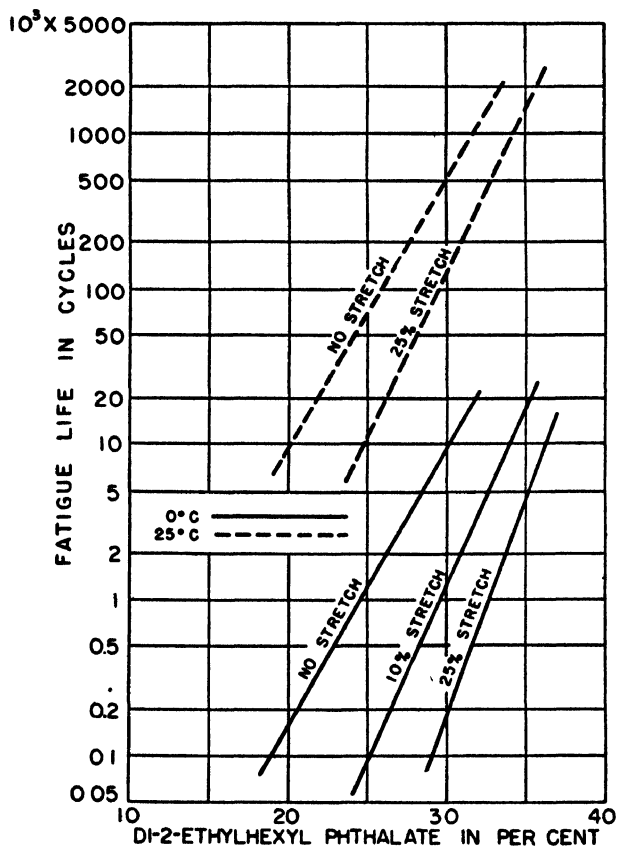


Figure 142. Fold-flex fatigue of stretched and unstretched "Vinylite" VYNW sheetings plasticized with di-2-ethylhexyl phthalate. (Adapted from Duggan and Fligor⁴⁸)

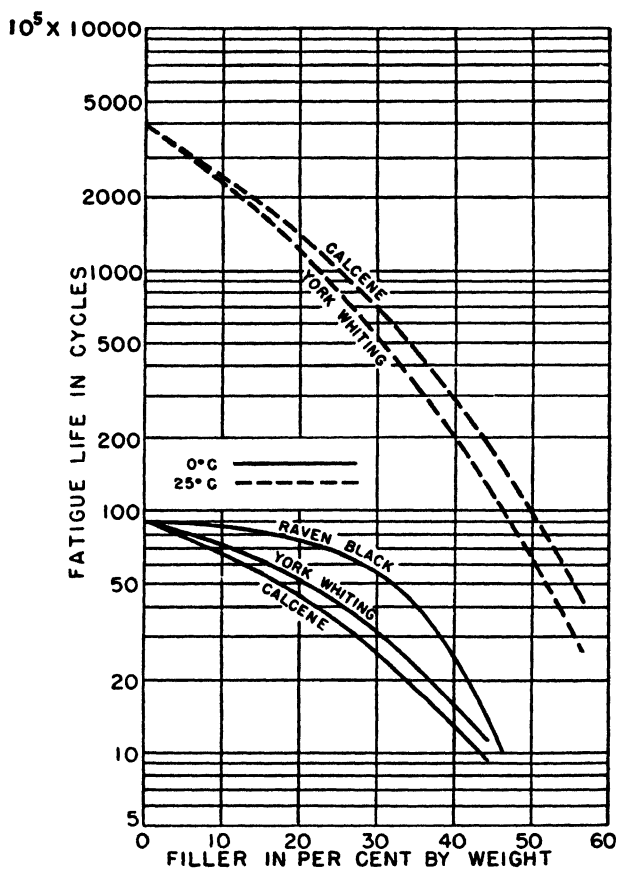


Figure 143. Fold-flex fatigue of variously filled "Vinylite" VYNW sheetings, plasticized to equal flexibility at 25°. (Adapted from Duggan and Fligor⁴⁸)

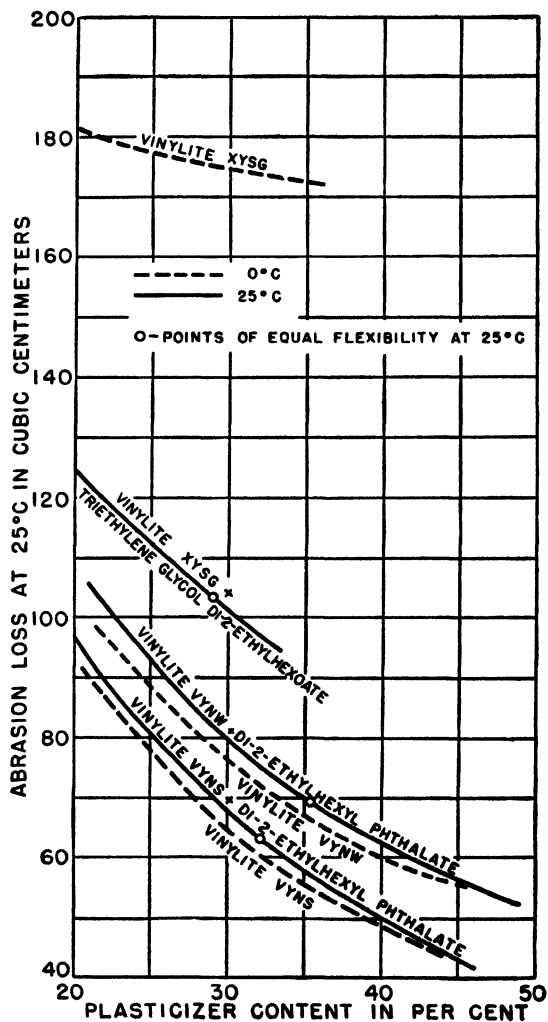


Figure 144. Effect of plasticizer content and temperature on abrasion resistance of various "Vinylite" resins. (Duggan⁴²)

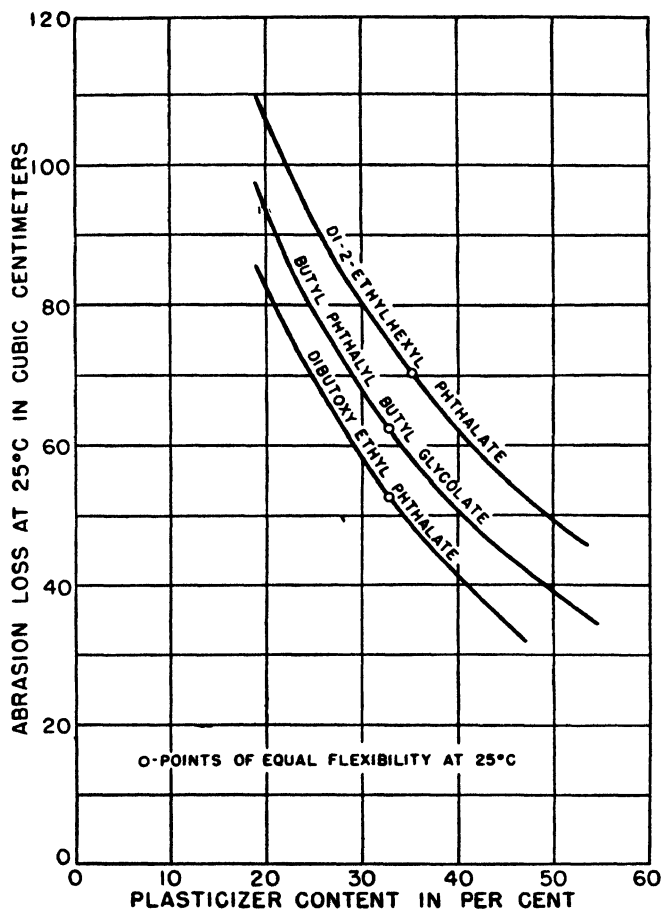


Figure 145. Effect of specific plasticizer as well as plasticizer content on the abrasion resistance of "Vinylite" VYNW. (Duggan ⁴²)

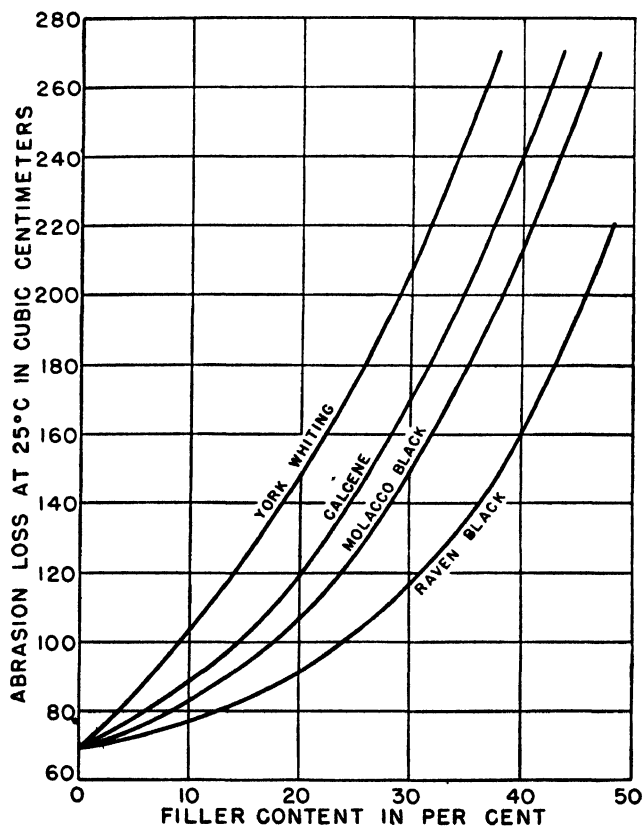


Figure 146. Effect of different fillers on the abrasion resistance of "Vinylite" VYNW plasticized with 35 per cent di-2-ethylhexyl phthalate, all vinyl compounds being equal in flexibility. (Duggan⁴²)

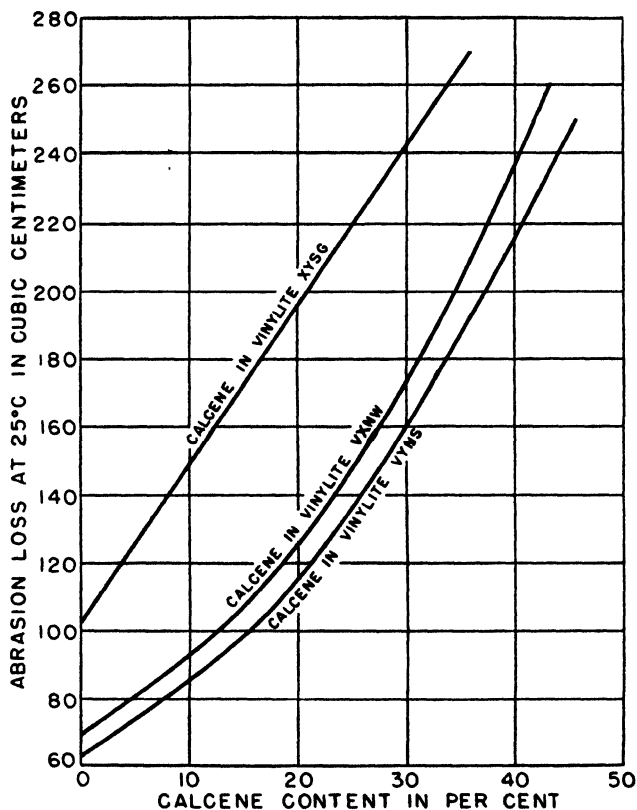


Figure 147. Effect of filler content on abrasion resistance of different "Vinylite" resins, all compounds being equal in flexibility at 25° and containing 28 per cent triethylene glycol di-2-ethyl hexoate, 35 per cent di-2-ethylhexyl phthalate, and 32 per cent di-2-ethylhexyl phthalate in the cases of XYSG, VYNW, and VYNS, respectively. (Duggan⁴²)

vary widely according to the nature of the particular resin and plasticizer used, Table 46 is included in order to give a general idea of the characteristics which may be expected of commercial calendered copolymer resin sheeting.

Table 46. Properties of a Typical Plasticized Hard Vinyl Copolymer Resin Sheetting *

Specific Gravity, 20/20°	1.26
Pounds per sq yd per mil thickness	0.059
Hardness (Shore Durometer A at 25°)	80
Water Extraction, per cent in 24 hr at 25°	0.20
Tensile Strength, lb per sq in	2800
Elongation, per cent at breaking point at 25°	325
Flammability	Slow burning †
Effect of Aging	Slight stiffening over long periods
Effect of Sunlight	Very slight darkening on long exposure
Fatigue Resistance	1,000,000 flexes

* Bakelite Corporation.

† The flammability and chemical resistance of plasticized sheeting are dependent upon the plasticizer.

Note: The physical properties of the sheeting are dependent upon the type and amount of plasticizer and the grade of resin used. The figures given are obtained with one of the standard types, VU-1930 Clear.

Molding Compositions. Plasticized hard vinyl chloride resins can also be molded by either compression or injection methods to yield elastomeric shaped articles. Numerous industrial and military applications of moldings of this type have been made, among which aircraft grommets are typical. Filled with powdered cork, plasticized molded polyvinyl chloride has found an interesting industrial application in rayon spinning cots.

Film Casting or Coating. Plasticized polyvinyl chloride has been applied from solution to numerous fabrics in the production of so-called "Korosealed" fabrics.

These products were just becoming of considerable importance before World War II. Industrial applications include corrosion-resistant liners for chemical conduits and coated or impregnated asbestos tape for electrical applications. Consumer uses are varied, including umbrellas, raincoats, tableclothes, bath caps, shower curtains, drapes, upholstery, and gloves.

Plastisols and Organosols. A remarkable new technique in fabrication of vinyl copolymers has been introduced with the development of pastes prepared by dispersion of finely powdered hard copolymer resin in suitable plasticizers. These pastes may be solvent-free possessing a consistency such that they can be readily applied as coating materials to fabrics or other surfaces. They can also be loaded into inexpensive molds which can be closed under low pressures. Dip-coating and open-curing

can also be practiced. Heating to temperatures of 160° causes the plasticizer to diffuse throughout the resin particles, resulting in a coherent plasticized sheet or solid article. Inasmuch as no polymerization occurs during this process and either no solvent or very little is present, there is substantially no decrease in volume. The pastes, themselves, are stable for many months at room temperature.

Products of this kind, made of "Vinylite" resins and containing no solvent, are available on the market under the name "Plastisols." Similar materials containing small amounts of solvent which can be removed during heating without appreciable volume change are available under the name "Organosols" and are especially useful for fabric coating purposes. Thick coats of vinyl resin can be applied in a single operation.

Miscellaneous. Miscellaneous forms of polyvinyl chloride include foam and sponge.

Because of the fact that polyvinyl chloride lacks unsaturation, sulfur exercises no vulcanizing effect upon it, although in combination with sodium sulfide, presumably as sodium polysulfide, it effects cross-linking of the linear chains. This latter reaction does not seem to have been used.

In Germany, polyvinyl chloride has been further chlorinated by substitution and spun into textile fibers under the name "PeCe." Because of the low softening point, use of this material has been confined largely to chemical filter cloth for which application its resistance to corrosive liquids makes it well adapted.

A significant new development in vinyl chloride resins is their production and distribution in the form of "Geon" latex of approximately 50 per cent solids content which is used in coating, impregnating, and film-forming applications.

Solutions of polyvinyl chloride, such as "Korolac," are available for various uses.

Polyvinyl chloride will dissolve in a limited number of solvents at the boiling point, but gels on returning to room temperature. Based on this fact, gels are commercially available ("Korogel") which can be warmed until they become liquid solutions. They can then be used as dipping baths to coat electroplating racks and other equipment which must be protected from corrosive chemicals. Chemical adhesion of the coating is relatively slight; union is effected by mechanical shrinking of the coating around the covered object.

Hard vinyl resins are compatible with butadiene-acrylonitrile copolymers such as "Buna N" and "Hycar OR." Such mixtures have been found highly useful in fabric coating compositions because of improved resistance to heat and solvents, with or without vulcanization of the elastomer. Excellent adhesives can also be prepared from such mixtures.

Trade Names and Prices of Hard Vinyl Resins

Hard vinyl resins are available in bulk form as follows: polyvinyl chloride under the trade-mark "Vinylite" QYNA from the Bakelite Corporation and under the designation "Geon" 100 Series (a name which has replaced "Koron") from the B. F. Goodrich Company. "Geon" latex is also available from the latter company. Copolymer resin possessing an approximate vinyl chloride content of 95 per cent and an apparent average Staudinger molecular weight of 22,000 is sold by the Bakelite Corporation under the trade-mark "Vinylite" VYNW.

These resins are converted into numerous finished elastomeric forms by a considerable number of fabricators, many of whom have their own trade names for their products, a complete catalog of which cannot be given here. "Koroseal" is especially worthy of mention because it pioneered in this field.

In 1945, these resins were priced at about 38 cents per pound, unplasticized, in carload lots.

Soft Vinyl Chloride Resins. Soft vinyl chloride resins, containing less than 92 per cent vinyl chloride, are manufactured for use primarily in unplasticized rigid moldings, sheets, textile fibers, and monofilaments, and for solution coating applications. They are produced by the Carbide and Carbon Chemicals Corporation and marketed by Bakelite under the trade-mark, "Vinylite" V series, in five principal grades, the composition and major uses of which are listed in Table 47.

Table 47. Grades, Composition, and Important Applications of Vinyl Chloride-Acetate Copolymer Resins

"Vinylite" Designation	Composition in % Vinyl Chloride	Average Apparent Molecular Weight (Staudinger Method)	Principal Applications
VYLF	85-88	6,000	Surface coatings
VYHH	85-88	10,000	Surface coatings Coated paper Phonograph records Floor tile Molding compounds
VMCH	85 (1% maleic acid)	10,000	Surface coatings
VYNS	88.5-90.5	16,000	Sheet stock
VYCF	88-90	16,000-19,000	Staple fiber
	88-90	20,000-23,000	Continuous filament
VYNW	96	24,000	Calendered sheeting Wire and cable coating Plastisols and organosols

The earlier discussion of the general properties of vinyl chloride resins is applicable to soft copolymers as well as to hard resins. The chief points of difference between these two groups have already been mentioned.

They are to be found in the lower softening points of the former, in their greater solubility in ketonic solvents, and in their adaptability to molding and spinning, without addition of external plasticizer. Like hard resins, these soft counterparts also require thermal stabilization with the same types of chemicals previously described. Unlike hard resins, however, plasticization is not employed except in solution coatings. Fillers, coloring materials, and lubricants may or may not be compounded with them, according to the application.

Uses of Soft Vinyl Chloride Resins

Surface Coatings. During recent years there has been a marked expansion in the use of vinyl resins for surface coating applications. Much of this development can be accounted for by the evolution of inexpensive ketones. Soft resins are used in vinyl lacquers in order to obtain satisfactory adhesion. Baking on metal surfaces at temperatures above 350° F is required, except in the case of a tripolymer discussed later. Because of the need for baking, thermal stabilization of vinyl chloride resins destined for use in coatings is particularly important.

Surface coatings must be formulated with resins of low enough molecular weight to yield non-viscous solutions of reasonable solids content, that can be easily applied by dipping, rolling, or with the use of a knife or rotogravure press. Application by brushing is more difficult. Vinyl copolymers possessing average apparent Staudinger molecular weights of 10,000 or less are therefore preferred. Various grades can be admixed for coating purposes. Toughness, strength, and chemical resistance of coatings, however, increase with increasing molecular weight and increasing vinyl chloride content, so that special lacquer applications may require higher viscosity copolymers. Table 48 shows the resistance to various solvents and chemicals of a typical soft vinyl chloride resin coating.

Ketones are excellent solvents for soft vinyl copolymers and are commonly used in lacquer formulations. Nitroparaffins are good solvents, esters only fair. Certain chlorinated hydrocarbons are often effective, but are not widely used in surface coatings because of toxicity. Aromatic hydrocarbon diluents may be utilized in lacquer formulation but especial attention must be directed to avoid excessive increase of viscosity, as well as gelation. Figure 148 illustrates the manner in which replacement of active solvent by diluent results in higher solution viscosity. This effect is most pronounced in concentrated solutions. A typical viscosity phase diagram of solutions of "Vinylite" VYHH in mixtures of methyl isobutyl ketone and toluene is shown in Figure 149.

Plasticizers are usually incorporated in surface coatings based on

Table 48. "Vinylite" Resin Properties*

<i>Mineral Acids</i>		<i>Solvents and Diluents</i>	
Dilute	Excellent—no attack	Alcohols and polyalcohols	Excellent—no effect
Concentrated †	Excellent	Ketones	
<i>Organic Acids</i>		Lower boiling ketones	Dissolve readily
Formic, acetic, propionic acids, etc.—Generally poor—concentrated acids soften lower polymers readily, dilute acids less readily		Higher boiling ketones	Swell or dissolve
		Aldehydes	Soften or dissolve
		Esters	Soften or dissolve
		Ethers, poly-ethers, and ether-type compounds	
<i>Alkalies</i>		Diethyl ether	Slight softening
Sodium or potassium hydroxides—all solution strengths		β, β' dichlorethyl ether	Swells.
Ammonium hydroxide		Diethyl "Cellosolve"	Swells
		Dioxane	Dissolves
		Propylene oxide	Dissolves
		Carbon disulphide	Swells
		Carbon tetrachloride	Good
		Chlorinated hydrocarbons, such as ethylene dichloride, monochlor benzene, etc.	
<i>Miscellaneous Corrosive Chemicals</i>		Glycol-ethers	Dissolve or swell
Phenol, resorcinol, cresol, etc.	Poor—soften	Hydrocarbons	Swell
Iodine, crystals	Fair—slight stain	Aromatics—benzene, toluene, etc.	
Iodine, tincture	Excellent	Aliphatics	Swell—dissolve lower polymers
Chlorine water	Excellent	Oils, fats, and waxes	Excellent—no effect
Bromine water	Excellent	Animal, mineral, and vegetable	Excellent—no effect
Potassium permanganate	Excellent		
Potassium dichromate	Excellent		
Silver nitrate	Excellent		
"Mercurchrome"	Excellent		
Hydrogen peroxide	Excellent		
Tannic acid	Excellent		

Note: Data applies to baked films of resin VYHH at 70° F. Higher molecular weight resins possess greater resistance to solvents and corrosive chemicals, especially at elevated temperature. Properties of compounds and coatings depend on type and amount of modifying material present.

* Bakelite Corporation.

† 66° Be' (96.5%) sulphuric, anhydrous hydrofluoric, and fuming nitric acids discolor resin VYHH.

vinyl resins. For general use, tricresyl phosphate and butoxyglycol phthalate ("Kronisol") are employed. Numerous other plasticizers can be utilized for specialized applications.

Except for iron and zinc pigments, which may catalyze thermal decomposition of inadequately stabilized films, almost all of the usual paint pigments can be utilized in vinyl copolymer lacquer formulation. Fig-

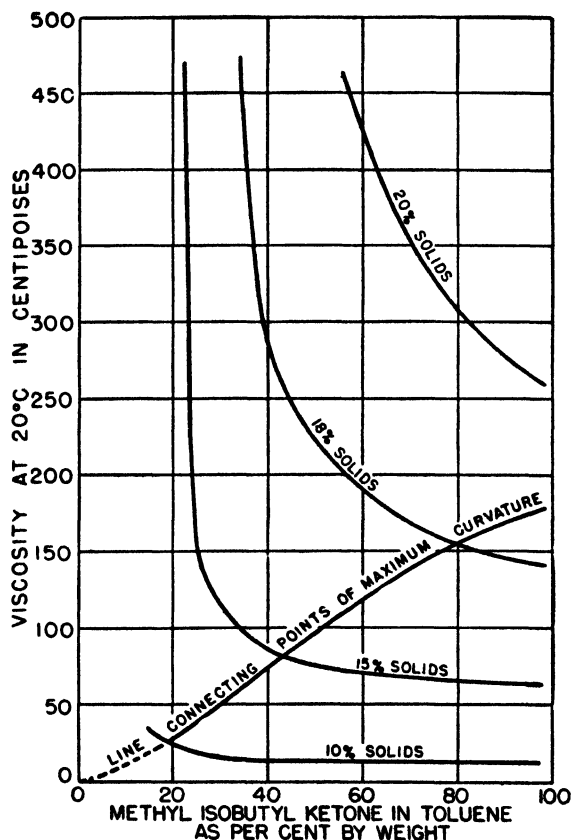


Figure 148. Equilibrium viscosities of methyl isobutyl ketone-toluene mixtures of "Vinylite" VYHH solutions.

Courtesy Carbide and Carbon Chemicals Corp.¹⁸

ments, however, are wet by these resins only with difficulty. They are, therefore, preferably admixed by the shearing action of a rubber mill. Pebble milling can be carried out also, with special precautions.

Vinyl copolymers are incompatible with most other resins, both natural and synthetic, so that they are usually employed as the sole resinous component of lacquers based thereon. A few exceptions to this general rule exist, notably in the case of polymethyl methacrylate. Various grades of vinyl copolymers can be blended.

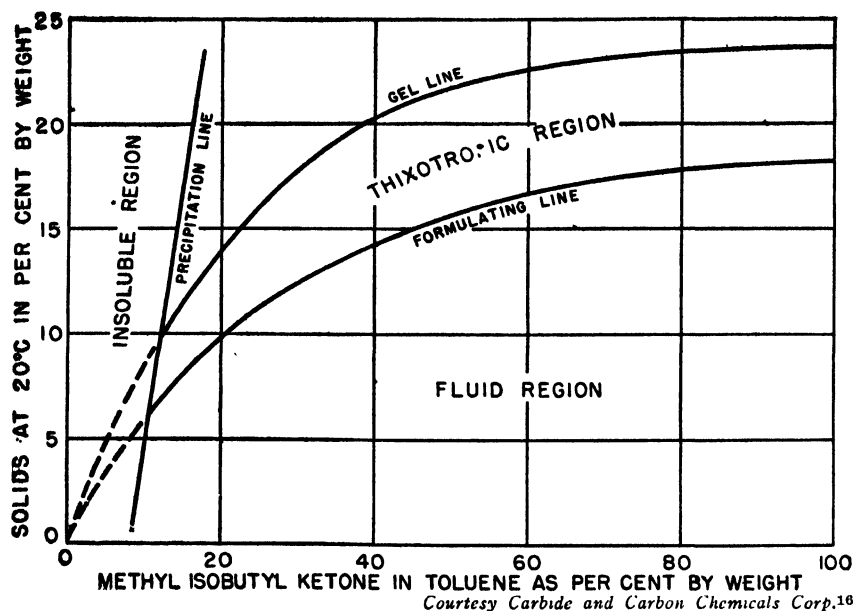


Figure 149. Phase diagram of solutions of "Vinylite" VYHH in mixtures of methyl isobutyl ketone and toluene.

Typical roll-mill formulas suggested by the Carbide and Carbon Chemicals Corporation¹⁶ are given below, in per cent by weight:

<i>Stock</i>		<i>Semi-Paste</i>	
	<i>Red</i>		
80	Cadmium red	70	Stock
15	"Vinylite" VYHH	30	Thinner *
4	Butoxyglycol phthalate	100	
1	No. 15 blown castor oil		
100			
	<i>White</i>		
68.5	Titanium dioxide	66.7	Stock
7.5	Antimony oxide	33.3	Thinner *
15.0	"Vinylite" VYHH	100.0	
8.0	Butoxyglycol phthalate		
1.0	No. 15 blown castor oil		
100.0			

* Thinner: 40 Methyl isobutyl ketone
10 Methyl *n*-amyl ketone
40 Toluene
10 Xylene
100

Optimum adhesion of vinyl copolymer resins is developed by baking. Air-drying alone is unsatisfactory except in certain specialized applications such as concrete coatings for swimming pools and the like.

Adhesion to metal surfaces is produced by baking at 350 to 400° F for times ranging from a few seconds in the case of metal foil, to an hour in the case of heavy steel plate. Top coats can be baked for shorter times at lower temperatures (275–300° F). Thermal decomposition during baking over iron or zinc surfaces is retarded by stabilization with the inhibitors discussed earlier, by separation from the metal surface by means of an intermediate primer coat of alkyd, phenolic, or other suitable resin, or by pre-treatment of the metal surface with phosphates, sulfides, or chromates, as in the "Bonderizing" process, to render the metal passive.

Table 49 lists a number of current applications of "Vinylite" lacquers, indicating the particular characteristics which fit them for the work at hand. A unique and invaluable property of well-formulated lacquers of this type is their adaptability to forming. Flat sheets of paper or metal coated with copolymer lacquers can be crimped, spun, punched, drawn, or otherwise shaped without injuring adhesion to the base material and without cracking the coating.

It has been pointed out that the use of copolymer vinyl chloride-acetate resins in surface coatings applied to metals requires baking, not only in order to eliminate solvent, but also to develop adequate adhesion. Baking temperatures are above the point at which thermal decomposition of the resin begins, so that incorporation of stabilizers or some kind of protection from the metal surface is necessary in such applications, especially where iron or zinc is involved. Lead pigments are satisfactory for this purpose, but in the formulation of clear, non-toxic coatings for such applications as liners for beer cans, they cannot be used and other expedients have been adopted. These problems have led to the evolution of a special type of vinyl resin capable of developing adhesion toward metal surfaces upon air-drying alone. This product, sold as "Vinylite" VMCH, is a tripolymer of vinyl chloride, vinyl acetate, and maleic acid. The ratio of chloride to acetate is approximately 85 to 14 and the maleic acid is present to the extent of one per cent. Molecular weight, estimated from viscosity measurements, is held as close as possible to an average value of 10,000.

Free carboxyl groups are thus present in small amount in the resin structure and these groups are capable of developing adhesion to metal surfaces at room temperature. With as little as 0.1 per cent acid, improvement of adhesion becomes apparent. With contents as high as 5 per cent, corrosion of the metal surface is encountered and decreased resistance to heat, light, and water begins to appear. For optimum balance of properties, it is often desirable to mix "Vinylite" VMCH with up to fifty per cent of its weight of another soft vinyl chloride resin.

Table 49. Surface Coating Applications of "Vinylite" Copolymers*

Application	Chemical Resistance (1)	Water Resistance	Oil and Grease Resistance	Alcohol Resistance	Non-toxicity (No Taste or Odor)	Resistance to Aging	Flexibility	Toughness	Forming(?) Qualities	Gloss — Wide Color Range	Heat Sealability
Metal Finishes											
Can Linings	X	X		X	X	X	X		X		
Collapsible Tube Linings	X	X		X	X	X					
Pail, Drum, and Tank Car Linings	X	X	X	X	X	X		X			
Flashlight and Storage Battery Coatings	X	X	X		X	X		X			
Ice Tray Coatings										X	
Laboratory and Hospital Equipment Finishes	X	X	X		X	X		X		X	
Metal Closure Finishes	X	X	X	X	X	X		X		X	
Metal Decorating Finishes	X	X	X	X	X	X		X		X	
Metal Foil Coatings	X	X	X		X	X	X	X		X	
Outdoor Sign Finishes	X	X	X		X	X		X			
Process Equipment Coatings	X	X	X	X	X	X		X			
Stop-off Lacquers for Electropainting	X										
Washing Machine and Refrigerator Finishes	X	X	X		X	X		X		X	
Textile Finishes											
Garment Label Adhesives	X	X			X	X	X				X
Permanent Textile Sires	X	X			X	X	X				X
Starcellac Collar Liners	X	X				X	X				
Waterproofing Finishes (Raincoats, Tents, Shower Curtains, Mattress Covers, etc.)	X	X	X		X	X	X	X		X	
Textile Printing Inks and Pastes		X	X			X	X	X		X	
Paper Coatings											
High Gloss Label Coatings		X	X	X						X	
Milk Bottle Closure Coatings		X	X	X	X	X			X	X	
Paper Container Linings	X	X	X	X		X			X		
Paper Tea Bag Adhesives	X	X	X	X							
Soap Wrapper Coatings	X	X	X								
Miscellaneous											
Chemically Resistant Inks	X	X	X	X	X					X	
Pulp Helmet Coatings	X	X		X		X				X	
Swimming Pool Finishes	X	X		X	X	X				X	
Wall Tile Finishes	X	X		X	X	X				X	
Coatings for Molded Phenolic Parts	X	X			X	X				X	

* Bakelite Corporation.

(1) See Table 48.

(2) Sheet metal or paper, coated in the flat, may be crimped, spun, punched, or drawn without cracking the "Vinylite" resin film.

Because of the presence of active carboxyl groups in this tripolymer, cross-linking and insolubilization with attendant increase of heat-resistance and hardness can be brought about by means of active pigments, such as blue lead or zinc yellow. Heat reaction can also be obtained with various synthetic resins containing active hydroxyl groups, such as surface-coating resins of the urea and melamine types. Reaction of this kind improves insolubility of coatings and increases water resistance. Addition of a small amount of phosphoric acid followed by baking further improves insolubility of such blends.

Vinyl tripolymer is also a useful base for primer coats applied before covering with high molecular weight copolymer resin, acrylate and methacrylate polymers, and Buna N type synthetic rubbers. It is especially meritorious in bonding the latter elastomers to metal.

Vinyl tripolymer has been found satisfactory as a base for coating materials applied to iron, steel, tinplate, terne-plate, galvanized iron, copper, brass, aluminum, magnesium, stainless steel, chromium plate, glass, cement, concrete, brick, tile, and plaster. Improvement of adhesion over that developed by copolymer resin has also been noted on paper, wood, cloth, and certain oil-base inks. Adhesion to painted surfaces is usually not increased.

Although excellent adhesion results from air-drying alone, further improvement results from low-temperature bakes which accelerate solvent release and development of ultimate hardness.

Rigid Sheets. Another important use of soft vinyl chloride resins is in exceptionally warp-proof, non-plasticized, rigid sheets. The higher molecular weight grades of soft copolymers are used for this purpose, as shown earlier in Table 47. Rigid vinyl copolymer sheets are available in a variety of transparent, translucent, and opaque colors, press-polished or matte-surfaced, and in thicknesses varying from 0.005 to 0.250 inch. Standard sheet size is 20 × 50 inches, but calendered material is also produced in 52-inch widths up to 0.015 inch thick. These sheets possess the chemical resistance shown in Table 48, exhibit low water absorption at room temperature, and are dimensionally stable, giving rise to almost no warpage. They may be formed upon heating by drawing, blowing, spinning, swaging, or shaping over mandrels. Machining operations such as punching, sawing, and shearing can be easily carried out. They can be printed with special inks.

Typical properties of rigid copolymer sheets are shown in Table 50, while characteristic applications are indicated in Table 51.

Molding Compounds. Molding compounds of soft vinyl chloride resins are available for compression and injection molding and for extrusion. They have not been widely used in the past except for phonograph

Table 50. Properties of Rigid "Vinylite" Sheets *

Odor	None
Taste	None
Tendency to Cold Flow	Slight
Forming Qualities	
Swaging, Shearing	Excellent
Blowing, Spinning	Fair
Specific Gravity, 20/20°	1.34-1.37
Specific Volume, cu in/lb	20.7-20.4
Refractive Index, N _d 20°	1.53
Softening Point, ° F	140-150
Water Absorption, per cent, 168 hr immersion at 25°	0.05-0.15
Flammability	Does not support combustion
Effect of Age	None
Effect of Sunlight	Darkens on prolonged intense exposure
Chemical Resistance	See Table 48
Tensile Strength, lb/sq in	8,000-10,000
Hardness, Brinell (550 lb-3 min)	12-15
Izod Impact Strength, ft-lb (notched specimen)	0.2-0.6
Modulus of Elasticity, lb/sq in	350,000-410,000
Modulus of Rupture, lb/sq in	10,000-13,000
Specific Heat, cal/° C/g	0.244
Thermal Conductivity, cal/sq cm/cm/sec/° C	0.000395
Linear Coefficient of Thermal Expansion per ° C	0.000069
Volume Resistivity at 30°, ohm-cm	Greater than 10 ¹⁴
Breakdown Voltage at 60 Cycles, volts per mil	650
Dielectric Constant at Radio Frequency	4.0
Power Factor at 1,000 Cycles	1.3%
Radio Frequency	1.7%

* Bakelite Corporation.

records, pocket combs, and toothbrush handles. These resins are the only ones which have been able to compete with shellac in the production of high-fidelity phonograph records, a unique application for which they are widely used. Flexible records for radio transcriptions are made of these resins. In the production of phonograph records is to be found one of the rare instances where a thermoplastic is loaded heavily with mineral fillers, like diatomaceous earth, which may constitute over half of the entire molding composition.

The presence of a trace of carboxylic acid groups in the tripolymer, "Vinylite" VMCH, mentioned in the discussion of surface coatings, has led to the interesting possibility of developing cross-linkages between resin chains by interaction with certain active metal oxides and sulfides, especially with lead compounds, like blue lead. Where intimate admixture is established by such operations as jet pulverization, compression molding of this resin with one of these mineral pigments results in the formation of exceptionally hard and heat-resistant products whose potentialities have as yet scarcely been touched.

Table 51. Applications for Rigid Vinyl Copolymer Sheets*

Application	Dimensional Stability (Will Not Shrink or Warp)	Non-flammability	Rigidity, Strength, and Toughness	Ease of Forming	Water Resistance	Chemical Resistance	Resistance to Aging	Accurate Printing	Wide Color Range	Clarity
<i>Aircraft</i>										
Enclosures	X	X	X	X	X		X			X
Frost Shields	X	X	X	X	X					X
<i>Automotive</i>										
Frost Shields	X	X	X		X					X
License Plate Protectors	X	X	X		X					X
Bookbindings—Comb Type	X	X	X	X				X	X	
<i>Charts</i>										
Aircraft and Navigation	X	X	X					X		
Recording	X	X					X	X	X	
Closures—Cosmetic Jar Sealer										
Disks	X	X			X		X	X	X	
Dials—Clock, Instrument, Radio	X	X		X	X		X	X		X
Display Forms—Transparent										
Electrical—Storage Battery Separators		X	X		X		X			
<i>Index Guides</i>										
<i>Instruments</i>										
Calculators	X	X					X	X		
Drafting Triangles	X	X	X				X	X		X
Printers' Gauges	X	X					X	X		X
Slide Rules	X	X	X	X			X	X		X
Windows	X	X	X	X	X		X	X	X	
Lighting Panels—Fluorescent	X	X	X	X			X	X	X	
Novelties—Advertising	X	X	X	X			X	X		X
Packages—Transparent	X	X	X	X	X		X	X		X
Patterns—Photo Templet	X	X	X	X			X	X		X
Plating Barrels	X	X	X		X		X	X		X
Playing Cards	X	X	X	X	X		X	X		X
Price Tag Holders	X	X	X	X	X		X	X		X
Radio Escutcheons and Windows	X	X	X	X	X		X	X		X
Recording Blanks	X	X	X		X		X	X		X
Signs	X	X	X							
<i>Trays</i>										
Luggage	X	X	X	X	X		X			X
Refrigerator	X	X	X	X	X		X			X
Watch Crystals	X	X	X	X	X		X			X

* Bakelite Corporation.

Textile Fibers. Fine filaments of vinyl copolymer are manufactured by passage of a resin solution through a spinneret and evaporating the solvent. Under the trade name "Vinyon," both staple fiber and continuous lengths are available in standard deniers in unoriented and oriented (cold-stretched) forms. Because of its relatively low softening point, "Vinyon" cannot be used in garments which will be subjected to laundering in hot water, but its chemical resistance has led to wide acceptance by the chemical industry as filter cloth. It is used in sail-cloth and rope, applications in which its mildew-resistance is of paramount importance. Numerous potential uses will undoubtedly be developed where heat-resistance is not a factor. Its low softening temperature is definitely advantageous in felt manufacture where it is matted with cotton fibers, then pressed while heated, making practicable the use of cotton in this application instead of rabbit's fur, formerly imported for the purpose. Table 52 gives a comparison of the tensile strength of "Vinyon" and other textile fibers.

Table 52. Strength Characteristics of "Vinyon" and Other Fibers *

Yarn	Dry (R. H. 65%)		Wet	Elongation (%)
	Tenacity (g/den.)	Elongation (%)	Tenacity (g/den.)	
Silk — degummed	4.22	15.7	3.40	26.3
Viscose	2.00	18.0	1.00	28.0
Acetate	1.40	27.0	0.85	36.0
"Vinyon" (1)	—	—	4.00	18.0
"Vinyon" (2)	—	—	2.30	25.0
"Vinyon" (3)	—	—	1.00	120+

* Manufacturers' data. Carbide and Carbon Chemicals Corporation.

Soft vinyl chloride copolymer monofilament similar to "Vinyon," but of greater diameter, is used as synthetic brush bristle.

A special spun plasticized fiber has been developed to exhibit reversible extensibility. It has found use in certain military and essential civilian goods and proved of particular value upon the disappearance of rubberized fabrics following Allied loss of the rubber plantations of the Far East. Typical applications are woven surgical stockings and knee braces.

Miscellaneous Applications. Other special products into which vinyl copolymers are fabricated include laminating foil for surfacing over printed matter or other areas which need to be protected from abrasion or scuffing and for the heat-sealing of garment labels and other emblems to be attached to cloth. Calender-coated paper has proved of especial merit in liners for closures of containers for food, beverages, pharmaceuticals, and toilet preparations.

A unique packaging process developed for the specific purpose of pro-

tecting ships and other military equipment in storage comprises the spraying of a "Vinylite" coating supported by filaments of saran. The latter resin is added as a webbing agent to a solution of the former so that, when emitted from a standard spray gun, a mesh of polyvinylidene chloride filaments is formed which supports a non-adherent, protective coating of "Vinylite" resin.

Miscellaneous Vinyl Chloride Copolymers

Other vinyl chloride copolymers are manufactured in Germany and are being developed in the United States. "Mipolam," produced by the I. G. Farbenindustrie A. G., is a copolymer of vinyl chloride and methyl acrylate. It is reported that similar products are being made in this country on a small scale.

Copolymers of vinyl chloride and vinylidene chloride are discussed in the next chapter. The oldest and best known representative of this family, "Saran," is produced by the Dow Chemical Company and is preponderantly vinylidene chloride. The "Geon" 200 series of resins made by B. F. Goodrich Company, however, are reported to be copolymers of these two unsaturated chlorides in which the vinyl derivative is present in greatest proportion. "Geon 202" appears to consist of approximately 94 per cent vinyl chloride and 6 per cent vinylidene chloride, while "Geon 203" is apparently built up from these monomers in the respective ratio of about 88 to 12.

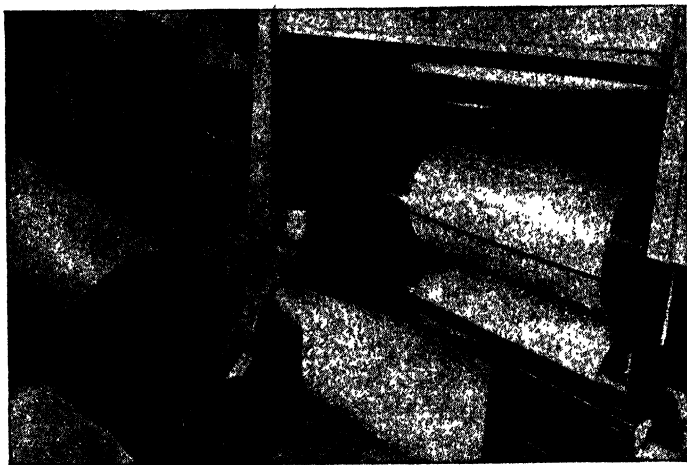
The Glenn L. Martin Company has recently announced its entry into the field of synthetic high polymers with the introduction of "Marvinol" vinyl resins. Products made therefrom range from rigid shapes to elastomeric bodies.

Polyvinyl Acetates

Several grades of polyvinyl acetate are manufactured by polymerization of monomer derived from acetylene. Because of the inhibiting effect of copper compounds, stills and columns used to purify the monomer may be made of copper to prevent polymerization during heating, but condensers and lines contacting the vapor should be of aluminum or stainless steel in order to prevent contamination of the finished product with stabilizing impurities.

As indicated earlier in this chapter, it is possible to vary the molecular weight of the product within wide limits by controlling conditions of polymerization. In commercial practice, temperature and duration of reaction are maintained as constant as possible from batch to batch and impurities are reduced to a minimum—usually 0.1 per cent or less. Viscosity of the product is controlled by varying the nature of the sol-

vent, the temperature of polymerization, and the nature and concentration of the catalyst. Toluene, for example, can be used as solvent for the



Courtesy Bakelite Corp.

Figure 150. Raw paper feed to a coating calender.



Courtesy Bakelite Corp.

Figure 151. Calender coating paper with "Vinylite" resin.

production of low-viscosity polymers, while benzene can be used for higher ones. Addition of controlled amounts of acetaldehyde can also be used as a means of varying the viscosity of the polymer, but is inadvisable

because of the poor light stability of the resulting product. At the end of the reaction, the solvent and unpolymerized vinyl acetate are removed and the resin is dried.

The highest molecular weight polyvinyl acetates are produced in aqueous emulsion by running monomeric vinyl acetate into a vigorously stirred slurry of water, catalyst, and colloidal emulsifying agent such as polyvinyl alcohol or hydroxyethyl cellulose.

Properties. Polyvinyl acetate resins are available in the solid form as colorless, thermoplastic, non-toxic solids which possess neither taste nor odor. Unlike the vinyl chloride resins, polyvinyl acetates are soluble in a wide range of organic liquids, including aromatic hydrocarbons and numerous oxygenated and chlorinated solvents. Their solubilities have already been listed in Table 43, where they are contrasted with the chemical resistance of vinyl chloride resins. Polyvinyl acetates are, however, insoluble in paraffinic hydrocarbons and for this reason can be used in coating paper to render it grease-proof.

The softening points of polyvinyl acetates range from 45 to 90°, or even higher in the case of polymers of highest viscosity. Some of the physical properties of various grades of polyvinyl acetate are listed in Table 53.

In general, because of their low softening points, polyvinyl acetates should not be exposed to temperatures above 150° F. As they tend to absorb water on prolonged exposure, they should not be used where constant immersion is necessary. They resist salt spray and dilute acids and alkalis, but concentrated acids and alkalies hydrolyze them to water-soluble polyvinyl alcohol.

Although incompatible with other vinyl polymers and with many synthetic resins, polyvinyl acetates can be readily compounded with many common plasticizers such as glycolates, phosphates, or phthalates of alcohols below C₈. Dibutyl phthalate is one of the best plasticizers for these resins, but di-2-ethylhexyl phthalate is unsatisfactory. Polyvinyl acetates are compatible with cellulose nitrate and low viscosity cellulose acetate propionate and acetate butyrate to which they are added in lacquer formulation to improve adhesion. They are also compatible with some of the oil-soluble phenolics, a few alkyds, condensation products of toluene sulfonamide and formaldehyde, certain rosin products like "Vin-sol," chlorinated rubber, chlorinated naphthalene (*i.e.*, "Halowax"), and a few natural resins like gum acaroid and mastic.

Uses. Polyvinyl acetates are not utilized as molding resins because of their relatively great cold flow and low softening points. Exceptions to this statement lie in their use as binders for wood flour in molded imitations of wood carvings and as binders for compositions heavily loaded

Table 53. Properties of "Vinylite" Polyvinyl Acetate Resins *

	AYAB	AYAA	Grades AYAF	AYAT	AYAW
Average Viscosity ⁽¹⁾ (seconds)	20 (45% Solids)	13.75 (20% Solids)	19 (20% Solids)	28 (20% Solids)	44 (15% Solids)
Softening Point ⁽²⁾ —°C	44	66	77	86.5	88.5
Form	Granular	Granular	Granular	Granular	Granular
Color	Water White	Water White	Water White	Water White	Water White
Burning Rate	Slow	Slow	Slow	Slow	Slow
Effect of Aging	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected
Effect of Sunlight	Unaffected	Unaffected	Unaffected	Unaffected	Unaffected
Heat Stability—Hours at 135°	1.15 (amber color)		No appreciable color change after 4.5 to 5 hours		
Water Absorption—					
% at 25°—16 hr	2.0	1.6	1.4	1.4	1.3
% at 25°—144 hr	7.3	4.0	3.6	3.6	3.4
Specific Gravity—20/20°	1.191	1.191	1.191	1.191	1.191
Tensile Strength—lb/sq in	⁽³⁾	1.500	2.600	4.200	4.600
Refractive Index n_D^{20}	1.4665	1.4665	1.4665	1.4665	1.4665
Per Cent Solids in Methyl Isobutyl Ketone at 110 ± 10 Centipoises					
Viscosity at 20°	41.5	27.5	21.0	18.0	12.4
Water Immersion ⁽⁴⁾	Swells, becomes pliable		Swells slightly	Only a surface attack, no penetration of water	

⁽¹⁾ Viscosity in seconds of aretone solution at 25° with No. 4 Ford Cup.⁽²⁾ Approximate values determined by modified ball and ring method.⁽³⁾ Impossible to break because of tendency to cold flow.⁽⁴⁾ Surface of all films immersed in water was unaffected after drying.

* Bakelite Corporation.

with mineral fillers employed in pressing out inexpensive advertising signs.

Some of the principal applications of the polyvinyl acetates are to be found in the adhesive field where they are used either in solution or emulsion, or as hot melts. Cellophane, cloth, paper, leather, wood, and other surfaces can be bonded therewith. The joints possess exceptional bond strength and are far superior in water-resistance, mold growth, and flexibility to those obtained with conventional adhesives based on such natural products as starch, dextrin, or hide glues. For use as a hot melt, low viscosity polyvinyl acetates are admixed with plasticizers or with other low-melting resins. This application has proved of especial merit in the manufacture of fiber containers and paper cups. Heat-sealing tape and film with the adhesive comprised largely of polyvinyl acetate are available for use in bonding paper and cloth and are particularly valuable in attaching cap liners and labels. Medium and low viscosity polyvinyl acetate solutions in ethyl alcohol or chlorinated hydrocarbons are used to strengthen food wrappers, to impart transparency to them, and to make them resistant to water and grease—characteristics of especial importance in this application.

Unlike most natural resins, polyvinyl acetates have a zero acid number and are therefore used in the formulation of non-tarnishing metallic inks, in inks for cellophane and glassine paper, in leather finishes, as binders for wood putty, as a component of chewing gum, as bonding agents for lenses, and as components of lacquers. They are favored in bookbinding and padding gums in which applications they have been found exceptionally meritorious, because, unlike hide glue, they yield flexible backings which do not embrittle with age and which do not require the use of fabric. Polyvinyl acetates are used as stiffening agents and sizes for paper and textiles. The exhaustion of aqueous emulsions used for the last two purposes is facilitated by addition of aluminum acetate or sulfate. In aqueous emulsions these resins are applied as primer surface coatings to tile, concrete, and ceramic articles which can later be lacquered or painted as desired.

The outstanding resistance of polyvinyl acetates to greases and oils adapts them to use in the coating of grease-proof paper in which field their heat-sealing properties may also be advantageous.

Certain limitations are imposed upon the use of polyvinyl acetates as the sole resinous constituents of lacquers and adhesives because of their tendency to cobweb and string. Precautions must be observed in applications on typical glue machines. Only the lowest viscosity grades of polyvinyl acetate can be applied by spraying because the higher types cobweb at reasonable solids content. Addition of nitrocellulose decreases cob-

webbing, while, on the other hand, polyvinyl acetate increases the adhesion and heat-sealability of the nitrocellulose.

Low molecular weight polyvinyl acetates in solid form tend to block in hot weather and at high relative humidities. Because of this characteristic and because of the cobwebbing tendencies of higher molecular weight grades, polyvinyl acetate coatings gained only limited acceptance before their introduction in the form of emulsions. High molecular weight polyvinyl acetates can be prepared in the state of emulsions of high solids content and low viscosity which can be sprayed without cobwebbing. With resins of sufficiently high molecular weight no blocking is encountered, although where plasticized sufficiently, even they will block. This difficulty can be eliminated by incorporation of a trace of an immiscible wax or oil like paraffin or castor oil. On evaporation of the water, an extremely thin film of the wax or oil is deposited upon the surface of the resin. If not used to the extent of more than one or two per cent, heat sealability is not seriously impaired.

Certain types of polyvinyl acetate emulsions, when properly applied, yield coatings that are as water-resistant as the corresponding lacquers, despite the presence of emulsifying agents in the film.

From 5 to 10 per cent of an organic solvent may be used in these emulsions. This relatively low amount of solvent presents no fire hazard and ensures smoothness of flow on baking.

Polyvinyl acetate is available in a range of viscosity grades under the trade-marks "Gelva," "Vinylite" A series, and "Elvacet"—formerly "RH" polyvinyl acetate. Prices in 1945 averaged 40 cents per pound in carload lots.

Solutions and emulsions are also on the market under such trade names as "Gelva," "Elvacet," and certain "Onyx Resin Dispersions."

Polyvinyl acetates modified by partial hydrolysis are available under the trade-mark, "Vinylseal," for special adhesive applications. These products are discussed in the section dealing with polyvinyl alcohol.

Various copolymers of vinyl acetate and other non-chlorinated unsaturates are available in Europe and are being explored in this country. "Povimal," a product of the I. G., is a copolymer of vinyl acetate and a maleic acid ester, for example. Copolymers of vinyl acetate and certain monomeric acrylics have been sold in limited amounts in this country as well as abroad.

Polyvinyl Ethers

Vinyl ethers can be polymerized by heat and by ultraviolet light, although less readily than the corresponding vinyl esters. Traces of

such catalysts as stannic chloride or antimony pentachloride cause polymerization with explosive violence. Metallic sodium is without effect. Polymerization proceeds smoothly under the catalytic influence of iodine, an interesting fact in view of the inhibiting action of this material in the polymerization of styrene, vinyl halides, and methacrylates. Degrees of polymerization ranging from 18 to 170 have been reported for polymers of vinyl ethers.

Vinyl ethers have been manufactured industrially in Germany by the I. G. and were polymerized to high molecular weight products sold under the names, "Igevin," "Lutonal," and "PV." Methyl, ethyl, and isobutyl ethers were available in several degrees of polymerization, ranging from viscous oils to wax-like solids. Most of these materials are glue-like masses which are either colorless or light yellow. Certain properties of typical polymers are listed below.

Table 54. Physical Constants of Polyvinyl Ethers⁵⁹

	Density (20°/4°)	Refractive Index (n_D^{25})	Dielectric Constant (50 cycles)	Volume Resistivity (ohm cm)	Power Factor (50 cycles)
Polyvinyl methyl ether	1.045	1.467	3.5	5×10^{12}	1×10^{-3}
Polyvinyl ethyl ether	0.96	1.454	3.0	6×10^{12}	2×10^{-3}
Polyvinyl isobutyl ether	0.91	1.452	2.2	1×10^{14}	1×10^{-3}

Polyvinyl methyl ether is readily soluble in cold water, but precipitates from aqueous solution at temperatures above 35°. Its solutions resemble those of starch and dextrin. Polymers of higher ethers are insoluble in water. The methyl ether is insoluble in aliphatic hydrocarbons, but higher ethers are soluble therein. The wide range of solubilities in organic solvents exhibited by these materials is shown in Table 55.

Polyvinyl ethers are compatible with several natural and synthetic resins used in the formulation of surface coatings, as shown in Table 56 on the next page.

Industrially, polyvinyl ethers have been used as textile sizes and finishing agents; as components of adhesives, especially pressure-sensitive adhesives; as thickening agents, particularly as additives for wood, fiber, and cable impregnants and insulating oils; as components of lacquers based on nitrocellulose and various natural resins to which they are added for improvement of adhesion and flexibility; and, in admixture with latex or aqueous dispersions of various synthetic resins, as treating agents for textiles, paper, and metal foil. Polyvinyl oleyl ether and copolymers with vinyl isobutyl ether have been reported to be pour-point depressants for mineral oils.

Certain vinyl ether copolymers are manufactured abroad.

Table 55. Solubilities of Polyvinyl Ethers ⁵⁹

Solvent	Polyvinyl Methyl Ether	Polyvinyl Ethyl Ether	Polyvinyl Isobutyl Ether
Water	+	—	—
Methanol	+	+	—
Ethanol	+	+	—
Butanol	+	+	+
Benzene	+	+	+
Toluene	+	+	+
Ligroin (100–140°)	—	+	+
Methylene dichloride	+	+	+
Carbon tetrachloride	+	+	+
Acetone	+	+	—
Cyclohexanone	+	+	+
Ethyl acetate	+	+	+
Butyl acetate	+	+	+
Methyl glycol ether	+	+	+
Ethyl glycol ether	+	+	+
Methyl glycol acetate	+	+	+
Ethyl glycol acetate	+	+	+
Turpentine	Difficultly soluble	+	+
Mineral oil	—		
Linseed oil	+	+	—
Castor oil	+	+	—
Tributyl phosphate	+	+	+
Tricresyl phosphate	+	+	—
Dibutyl phthalate	+	+	—

Table 56. Compatibilities of Polyvinyl Ethers with Various Resinous Materials ⁵⁹

Resin	Polyvinyl Methyl Ether	Polyvinyl Ethyl Ether	Polyvinyl Isobutyl Ether
Cellulose nitrate	+	+	—
Cellulose acetate	—	—	—
Benzyl cellulose	partially compatible	—	—
Polyvinyl acetate	—	—	—
Polymethyl acrylate	—	—	—
Polystyrene	+	—	—
Polyvinyl chloride	—	—	—
Rubber	—	—	—
Chlorinated rubber	partially compatible	—	—
Rosin	+	+	+
Shellac	+	+	partially compatible
Congo copal	+	+	+
Dammar	+	+	partially compatible

American production of polyvinyl ethers has thus far been confined to the developmental scale. The General Aniline & Film Corporation has recently announced the availability of monomeric methyl, *n*-butyl, and isobutyl vinyl ethers in limited amounts for experimental use. It is understood that research on their polymers is in progress in the laboratories of this company.

Secondary Vinyl Resins

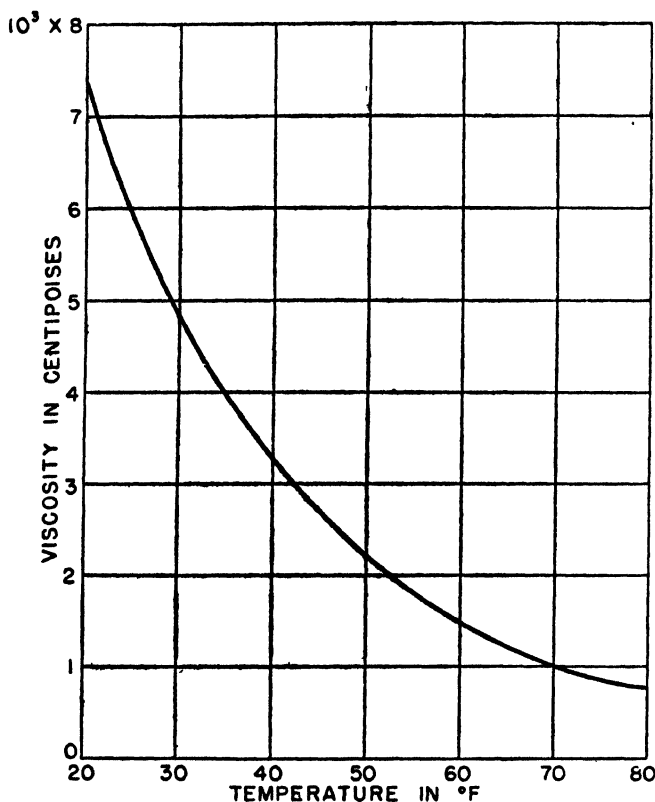
Polyvinyl Alcohol

Preparation and Types. Polyvinyl acetate is easily hydrolyzed in alcoholic solution by either acid or alkali. The former leaves traces of acid in the product which are very difficult to remove, so that the polyvinyl alcohol formed is partially dehydroxylated, probably because of catalytic dehydration during drying. In the case of alkaline hydrolysis, the product is contaminated with sodium acetate which must be removed by dialysis of the aqueous solution of the precipitate. Instead of hydrolyzing with either acid or alkali, polyvinyl acetate can readily be converted to polyvinyl alcohol by the process of alcoholysis. The acetate is first swelled in anhydrous methanol. The reaction is then catalyzed by addition of 0.5 per cent, or less, of caustic alkali in methanol solution. Acid may also be used as catalyst. Water, even in traces, should be avoided inasmuch as it impedes reaction. Polyvinyl alcohol gradually forms at room temperature, the acetate passing from the initial swollen state to a viscous solution and finally to an opaque gel. The total time of reaction approximates $1\frac{1}{2}$ hours with an alkaline catalyst. If the gel is dissolved in water and precipitated with acetone, polyvinyl alcohol is obtained. The product thus made still contains some 5 per cent of its acetate groups unchanged. By interrupting the alcoholysis at appropriate intervals, mixed alcohol-acetates can be obtained which possess any desired percentage of acetate radicals.

The properties and consequently the uses of polyvinyl alcohol depend upon the extent to which hydrolysis is carried out. Where polyvinyl acetates are modified by only partial hydrolysis so that from 85 to 70 per cent of the original acetate groups remain, the products are insoluble in water, but dissolve in such organic solvents as aromatic hydrocarbons and aliphatic esters. Where hydrolysis is carried further, so that the residual acetate radicals are reduced to about 35 per cent of the original number, solubility in organic solvents disappears, while the product dissolves in cold water, but precipitates on heating. When the residual acetate groups are still further reduced to 20 per cent of those originally present, the resin is soluble in both hot and cold water. Figure 152 typifies viscosity-temperature relations in aqueous solutions of this grade of polyvinyl alcohol.

Where hydrolysis is carried as far toward completion as possible, so that only 5 per cent or less of the original acetate groups remain, the resultant polyvinyl alcohol—oddly enough—only swells in cold water, but dissolves on heating.

Modified polyvinyl acetates of the type first described, wherein hydrolysis is only 15 to 30 per cent complete, are available under the trademark, "Vinylseal," in toluene and methyl acetate solutions. These adhesives possess superior shock resistance and yield excellent bonds with non-porous surfaces. They are especially serviceable in uniting metal



Courtesy E. I. du Pont de Nemours & Co., R. & H. Chemicals Dept.⁴⁵

Figure 152. Viscosity-temperature relation of an approximately 10 per cent aqueous solution of medium viscosity polyvinyl alcohol.

laminates, such as cores of small electric motors. Heat and moderate pressure should be used during bonding. They are also recommended for bonding glass and various plastics, including ureas and phenolics which usually present notoriously difficult cementing problems.

Resinous materials commonly called polyvinyl alcohol are more extensively hydrolyzed. In commercial products, depending on solubility type, from 65 to 95+ per cent of the acetate groups are removed. Under the trade names "Solvar" and "Elvanol"—formerly "PVA"—they are

manufactured in low, medium, and high viscosities and in various degrees of hydrolysis.

A portion of the structure of a polyvinyl alcohol in which all of the original acetate groups have been hydrolyzed may be represented as follows:



Properties. The outstanding property of commercial grades of polyvinyl alcohol is their water-solubility. They are also soluble in dilute aqueous salt solutions.

There is a critical concentration, characteristic for each salt, above which polyvinyl alcohol will not dissolve therein, as shown by Table 57.

Table 57. Minimum Concentrations of Salt Solutions in Which Polyvinyl Alcohol Is Insoluble ⁴⁵

Salt	Conc. of Salt Solutions at Which RH-391 Will Not Dissolve %
NaCl	20.0
Na ₂ SO ₄	3.0
KCl	20.0
K ₂ SO ₄	4.0
Na ₂ CO ₃	2.0
Al ₂ (SO ₄) ₃ · 18H ₂ O	10.0
Na ₃ PO ₄ · 12H ₂ O	4.0
K ₂ Al ₂ (SO ₄) · 24H ₂ O	7.0
(NH ₄) ₂ SO ₄	4.0
ZnSO ₄ · 7H ₂ O	6.0
Na ₂ SiO ₃ · 9H ₂ O	7.0
NaHCO ₃	10.0
(NH ₄)H ₂ PO ₄	7.0
(NH ₄) ₂ HPO ₄	5.0
Na ₂ S ₂ O ₃ · 5H ₂ O	7.0
Na ₂ SO ₃	3.0

Aqueous solutions of polyvinyl alcohols resemble starch solutions in many of their properties, but they are not attacked by bacteria and are seldom subject to fungus growth. Like starch, also, these polymers give a purple color with iodine. Polyhydric alcohols, acid amides, and analogous compounds dissolve or swell polyvinyl alcohols which can therefore be plasticized with high-boiling compounds of these categories.

As striking as the water solubility of polyvinyl alcohols is their resistance to most organic liquids. They are completely unaffected by oils, fats, or greases. They are highly resistant to hydrocarbons and to most organic solvents of the ester, ether, alcohol, and chlorinated hydrocarbon classes, as well as carbon disulfide. Their films possess neither taste nor odor. They are tough and highly impermeable to most gases.

Polyvinyl alcohols can be re-acetylated by heating with acetic anhydride and pyridine. They can also be esterified with other acids, acid chlorides, and anhydrides. By reaction with dicarboxylic acids or their derivatives, they can be rendered water-insoluble. Heat-treatment also reduces their solubility in water, as does reaction with formaldehyde or with copper and zinc ammonia complexes. Treatment with dichromates followed by exposure to light decreases water-solubility, a property of commercial utility.

Polyvinyl alcohols can be vulcanized by heating with sulfur to yield products somewhat resembling either soft or hard rubber in physical appearance, depending upon conditions. This process has not yet become of any practical significance.

Uses. Polyvinyl alcohol is used as a size for nylon, an application of considerable importance. It is recommended for use by the paper industry in the application of pigmented coatings, as an impregnant to increase wet strength, as a grease-proof coating material, and as a softener in the manufacture of glassine paper.

Other uses have been developed for polyvinyl alcohols as adhesives, pigment binders, and dispersing agents. Where either heat-sealability or emulsifying properties are desired, an alcohol containing from 20 to 35 per cent unhydrolyzed acetate groups is much superior to the completely hydrolyzed grade.

Protective films of polyvinyl alcohol, easily removed by washing in water, can be applied to electroplated surfaces and other highly polished metal areas. Impermeability to hydrogen sulfide makes the deposition of such transparent films a practicable method of preventing the tarnishing of store displays of copper and silverware.

Light-sensitive coatings consisting of mixtures of polyvinyl alcohol and dichromates can be applied to grained zinc plates and used in photolithic printing.

Compounded with suitable plasticizers, polyvinyl alcohol is fabricated into a variety of forms under the trade names "Resistoflex" and "Compar." It is extruded as seamless, flexible tubing, either plain or reinforced with braided fabric or wire. To prevent external softening by moisture it is available in neoprene-coated form. Such tubing is recommended for handling oils and greases, hydrocarbons, and chlorinated hydrocarbon solvents. It is used in hose for paint spray guns and in refrigeration units which operate with any anhydrous refrigerant except ammonia, by which it is attacked. Because of the water solubility of polyvinyl alcohol, these products are entirely unsatisfactory for handling water and aqueous solutions.

Greaseproof, but not waterproof, industrial gloves and work aprons,

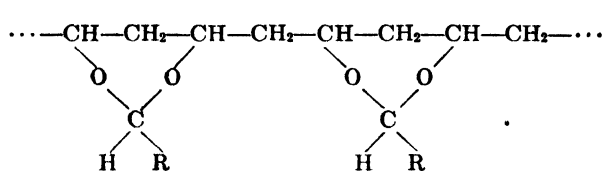
sheeting for gaskets and diaphragms, and miscellaneous molded shapes of "Resistoflex" are also available. Tensile strength of molded compounds is less than half that of extruded materials which averages about 5000 pounds per square inch.

Polyvinyl alcohol is inherently more expensive than polyvinyl acetate because it is derived from the latter material, about half the weight of which is lost as acetic acid upon hydrolysis.

Polyvinyl Acetals

Polyvinyl acetate can be converted to polyvinyl acetals by intermediate transformation to the alcohol and subsequent reaction with any desired aldehyde. Because of the 1,3-relationship of the hydroxyl groups, cyclic acetals appear to be the primary reaction product, as in the case of simple

1,3-glycols. If the aldehyde is designated as $R-C \begin{smallmatrix} H \\ // \\ O \end{smallmatrix}$, and other types of acetals which probably form to a minimum extent are overlooked, the corresponding resin possesses the following formula:



Acetals can also be produced from polyvinyl acetate directly by reaction with an aldehyde in 95 per cent ethanol, for example. If desired, a simple polymer like paraldehyde can be used instead of the aldehyde itself. Reaction is brought about by means of a catalyst favoring acetal formation, such as concentrated hydrochloric acid, calcium chloride, or zinc chloride. Incorporation of such stabilizers as *p*-ter-amylphenol during acetalation improves the resistance of the product to thermal discoloration.

However acetalation is carried out, the products are only partial acetals because the acetate radicals of polyvinyl acetate cannot be removed completely by either type of reaction. The degree of acetalation can be controlled in both instances, so that partial acetals having various ratios of acetate, hydroxyl, and acetal groups are obtainable. The properties of the products vary not only with the nature of the aldehyde and the molecular weight of the resin, but also with the degree of acetalation. In general, viscosity, insolubility, and strength characteristics increase with increasing molecular weight of the polyvinyl acetate used and with the degree of acetalation.

Polyvinyl Formal. Polyvinyl formal, produced by reaction of polyvinyl acetate with formaldehyde, is available from Shawinigan Products Corporation under the trade-mark, "Formvar." The grade is designated by a double number; the first one representing the viscosity of the original polyvinyl acetate from which it was made, the second one corresponding to the degree of acetalation. Although several grades have been made experimentally, "Formvar 15-95," E resin, is the only one available at present. It is priced at about 75 cents per pound in carload lots. Typical properties of this product in molded form are given in Table 58.

Table 58. Properties of "Formvar 15-95" E Type *

Physical properties:	
Color	light straw
Density	1.23 (20°/25°)
Refractive index	1.50 (n_D^{20})
Specific volume	22.5 cu in/lb
Working properties:	
General type	thermoplastic
Molding qualities	must be compounded
Molding conditions	150-170° at 2000-3500 lb/sq in
Tendency to cold flow	none
Extruding qualities	must be compounded
Thermal properties:	
Burning rate	burns slowly
Effect of heat	stable to 150°
Softening point	about 190°
Thermal conductivity	37×10^{-6} cal/sec/cm ² /°C/cm
Thermal expansion	7.7×10^{-5} /°C
Heat distortion	100-125°
Mechanical properties:	
Tensile strength	10×10^3 lbs/sq in
Electrical properties:	
Breakdown voltage at 30°	1200 v/m
Dielectric constant at 30°	3.7
Power factor at 30°	0.007
Physical chemical properties:	
Effect of sunlight	very slight
Effect of ultraviolet	very slight
Effect of aging at room temp.	very slight
Water absorption A.S.T.M., 48 hrs	1.3%
Abrasion	700-800 (Schuh abrasimeter)

* Manufacturers' data. Shawinigan Products Corp.

"Formvar" is soluble in dioxane, ethylene dichloride, 60/40 toluene-alcohol mixture, and in various ketones, chlorinated hydrocarbons, and amines. It is insoluble in alcohols, ethers, and both aliphatic and aromatic hydrocarbons. It is compatible with certain phenolic resins, chlorinated biphenyls and naphthalenes, cellulose nitrate, and toluene sulfonamide-formaldehyde condensation products. It is incompatible with most other resins.

The most important application of polyvinyl formal to date has been in approximately 1:2 combination with phenolic resins in electrical insulation for magnet wire. Because of the high viscosity of solutions of this resin, wire cannot be economically coated with it by conventional methods. Use of a floating die maintained concentric with the wire by the wire itself has therefore been developed for large-scale manufacture of "Formvar"-coated wire, sold under the trade name "Formex." This lacquer is equally as good an insulator as the conventional alkyd coating of enameled wire. It is markedly superior in flexibility, extensibility, resistance to abrasion and mechanical abuse, and other toughness characteristics. "Formvar"-coated wire is therefore particularly well-suited to mechanical winding. "Formex" wires can be twisted together tightly and handled on modern high speed winding machines without danger of injury to the coating. One objection encountered with "Formex" wire, but not met in enameled coatings is to be found in the fact that strains are introduced into the resinous coating by bending. Upon subsequent immersion in a liquid, such as high flash naphtha, these strains result in immediate formation of cracks. This difficulty can be overcome to a considerable degree by relieving the strains through suitable heat-treatment, a process physically comparable to the annealing of glass although it is, of course, carried out at much lower temperatures—in the order of 100°.

Because of the transparency of polyvinyl formal films, "Formex" magnet wire possesses the color characteristic of copper itself and can be distinguished from enameled wire by this means.

"Formvar" has also been used in laminating and coating wooden propellers for aircraft. It is noteworthy that this resin is the only thermoplastic which has been found satisfactory for this purpose. Another important military application has been as the inner gasoline-resistant liner of bullet-proof tanks for airplanes. Both of these uses have been developed in England. A number of other military applications of the resin have also been made.

Polyvinyl Acetal. Polyvinyl acetal is produced commercially by Shawinigan Chemicals, Ltd., under the trade-mark "Alvar" in a variety of grades, depending upon the viscosity of the initial acetate and the percentage acetalation, as in the case of "Formvar."

These resins are odorless and tasteless. Table 59 gives typical properties of these products.

Polyvinyl acetals are soluble in a wide range of alcohols, ketones, esters, and chlorinated hydrocarbons. They are insoluble in aliphatic and aromatic hydrocarbons and in vegetable oils. They are incompatible with cellulose acetate, ethyl cellulose, polystyrene, and chlorinated rubber,

Table 59. Physical Properties of Polyvinyl Acetals *

Grade of "Alvar"	Softening Point
5-80	158°
7-70	153°
11-90	195°
15-70	178°
15-80	185°
Physical properties:	
Color	light straw
Specific gravity	1.16 (20°/25°)
Refractive index	1.46 _D ²⁰
Specific volume	23.8 cu in/lb
Thermal properties:	
Burning rate	burns slowly
Effect of heat	stable to 150°
Heat distortion	75°-90°
Softening pt	135°-190°
Specific heat	0.29 cal/°C/g
Thermal conductivity	44×10^{-5} cal/sec, cm ² , °C/cm*
Thermal expansion	6.5×10^{-5} /°C
Mechanical properties:	
Tensile strength	6,000-9,000 lb/sq in
Electrical properties:	
Breakdown voltage at 30°	950 v/m
Dielectric constant at 30°	2.8
Power factor	0.007
Physical chemical properties:	
Effect of sunlight	slight
Effect of ultraviolet	slight
Effect of aging at room temp.	slight
Effect of water	slight
H ₂ O absorption after 24 hr	2%
Acid number	0.5-1
Working properties:	
General type	thermoplastic
Molding qualities	good
Molding conditions	
Temperature	125-150°
Pressure	500-2,000 lb/sq in
Extruding qualities	good
Hardness:	
Exceptionally hard and tough. Not scratched with an 8H pencil under 300 gram load.	
Abrasion results also very high. Schuh abrasimeter 500-650.	

* Manufacturers' data. Shawinigan Products Corporation.

but can be incorporated with most other synthetic resins either by milling or solution.

Polyvinyl acetals have found limited applications in surface coatings for indoor use, especially in combination with nitrocellulose with which they are compatible in all proportions. They have been used in molding compounds, especially in shoe-heels, phonograph records, floor and roofing

tile, grinding wheels, and printing plates, although these applications have thus far been limited in volume. Some use has been made of "Alvar" injection molding compounds in bottle closures and toilet articles, especially fine-toothed combs. These resins are tough, easy to mold, are unplasticized, and fill up fine detail in the mold with accuracy.

Polyvinyl acetal, like the acetate, is used as a binder for wood flour in molded artificial wood carvings and signs.

Polyvinyl Butyral. Like other polyvinyl acetals, the butyral can be manufactured either by reaction of butyraldehyde with polyvinyl alcohol, or by direct reaction of the aldehyde with polyvinyl acetate in the



Figure 153. Reaction kettles used in one of the steps in the manufacture of "Butacite"

*Courtesy E. I. du Pont
de Nemours & Co.*

presence of a suitable catalyst. Inasmuch as the preferred form of this plastic for use as safety glass interlayer contains an appreciable proportion of free hydroxyl groups, reaction of polyvinyl alcohol with butyraldehyde is the common commercial practice. Products are available on the market under the trade names "Vinylite" X, "Butacite," "Butvar," and "Saflex." Where used in safety glass construction, this plastic is commonly known as "Vinal."

Polyvinyl butyral resins were developed specifically for safety glass application because of their adhesive characteristics, their toughness, clarity, and extensibility where properly plasticized. Their molecules comprise not only butyral groupings, but also a small number of acetate groups, unavoidably present because complete hydrolysis of polyvinyl acetate cannot be accomplished, and a relatively large proportion of hydroxyl radicals which play a very important role in the development

Properties

Typical physical properties of polyvinyl butyral resins are given in Table 60.

Table 60. Properties of Polyvinyl Butyral Resins *

Specific gravity, 20/20°	1.11
Tensile strength, lb/sq in	8100-8500
Notched impact, ft lb per specimen (.5 × .5 bar .1 in notch)	0.44-0.60
Modulus of rupture—lb/sq in	11,400
Heat distortion point (A.S.T.M.°)	57-58
Water absorption—16 hr at 60° (A.S.T.M.)	3-5%
Resistance to alkalis	Moderately good
Resistance to acids	Poor

* Bakelite Corporation. The properties shown here are those of "Vynlite" Resin XYSG.

Although insoluble in water, these resins are hydrophilic because of their hydroxyl content. Because of this characteristic, they exhibit good adhesion toward glass which also is hydrophilic. For this reason, unlike older types of safety glass, vinyl interlayer can be bonded directly to the glass sheets without the use of an intermediate adhesive. In general, hydrophilic surfaces should be bonded with hydrophilic resins in order to obtain optimum adhesion. The production of a water-resistant bond is contingent upon a careful balance between hydrophilic properties and water insolubility. Fragments of windshields broken by collision remain attached to the interlayer, rather than breaking loose to present a dangerous hazard.

Because of the great extensibility of properly plasticized polyvinyl butyral sheeting, when breakage of safety glass made from it does occur, the glass cracks into small sections which adhere to the interlayer and the whole broken panel is distended, thus absorbing the energy from the blow gradually. This is an important property in preventing injury to head or shoulders which may be thrown against a windshield by collision.

Because of the adhesion and water-insolubility of this plastic, coupled with the non-volatile character of the plasticizers employed, it is unnecessary to seal the edges of safety glass built therewith. Manufacturing costs are thus reduced and fabricated sheets can also be readily cut to shape on the job by first breaking each pane of glass, then cutting the interlayer with a razor edge.

For the development of extensibility and flexibility, polyvinyl butyral is always plasticized. The best plasticizers are purely aliphatic in nature. Triglycol 2-ethyl butyrate ("Flexol" 3GH), triglycol 2-ethyl hexoate ("Flexol" 3GO), and dibutyl sebacate are particularly valuable and are used in the ratio of some 30 parts of plasticizer to 70 parts of

resin, by weight. Table 61 shows typical properties of plasticized polyvinyl butyral sheeting.

Table 61. Properties of "Vynlite" Highly Plasticized Resin Sheeting *

Properties	Series X Sheet †
Specific gravity	1.11-1.12
Specific volume, cu in/lb	24.8-25.0
Water absorption, % in 24 hr at 25°	3.0-5.0
Tensile strength, lb/sq in	3,000-3,500
Elongation, %	250-275
Flammability	slow-burning
Effect of age	none
Effect of sunlight	none

* Bakelite Corporation.

† Safety glass interlayer stock (XU-1315 natural).

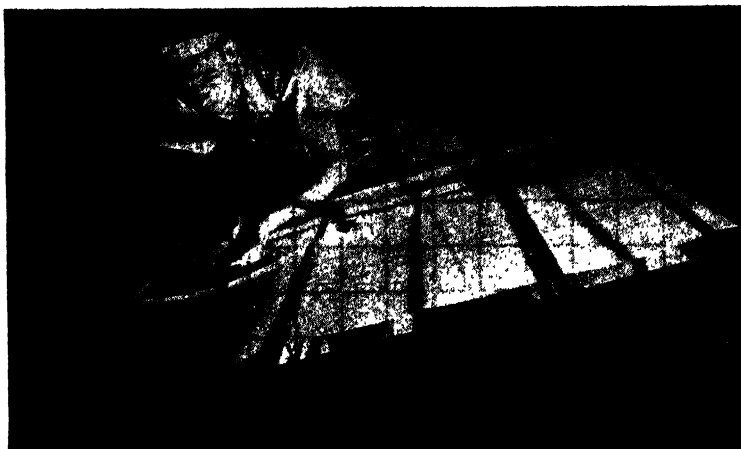
Uses

Plasticized polyvinyl butyral sheeting is vastly superior to the older types of plastics used in safety glass, namely: cellulose nitrate, cellulose acetate, and polymethyl acrylate. It is some ten times as resistant to rupture at -10°F and four times as resistant at 70°F as are equivalent thicknesses of other types of safety glass. Its superiority is shown graphically in Figure 157; one of its most outstanding merits, therefore, is a very substantial increase in safety of driving during cold weather.

Safety glass sheeting is made either by calendaring or by extruding as a thick solution, evaporating the solvent subsequently. Laminated glass itself is made from plastic sheeting by inserting the latter between two carefully cleaned glass plates and bonding under heat and pressure to eliminate air pockets and consummate adhesion. This operation is usually carried out under pressure in an autoclave.

Safety glass interlayer is now produced in a standard 0.015 inch thickness. Heavier sheeting is available for use in laminated glass for sub-stratosphere aircraft. Such glass is made from sheeting which protrudes beyond the edges of the glass panes and which, sometimes built up to greater thickness by supplementary layers of plastic around the outer edges of the glass, provides a means of effecting an hermetic seal of aircraft cabins without introducing strains that might lead to fracture of the glass. Pressure-tight laminated glass of this kind is available under the trade name "Flexseal."

A most important innovation in this field has been the development of "Metal Insert Flexseal," in which a continuous light metal strip, approximately 1/32 inch in thickness, is incorporated in the layer of polyvinyl butyral plastic, thus providing greater edge rigidity, especially at elevated temperatures. By rounding the glass corners and omitting the



Courtesy E. I. du Pont de Nemours & Co.

Figure 155. Continuous "Butacite" sheeting passing through an air cooling process.



Courtesy Monsanto Chemical Co.

Figure 156. Winding continuous length polyvinyl butyral film.

metal around them, rigidity is lessened, resulting in elimination of corner breakage. A still further marked improvement of this unit has been evolved in "Slotted Metal Insert Flexseal," wherein metal edging of the discontinuous type is slotted in order to provide a series of discon-

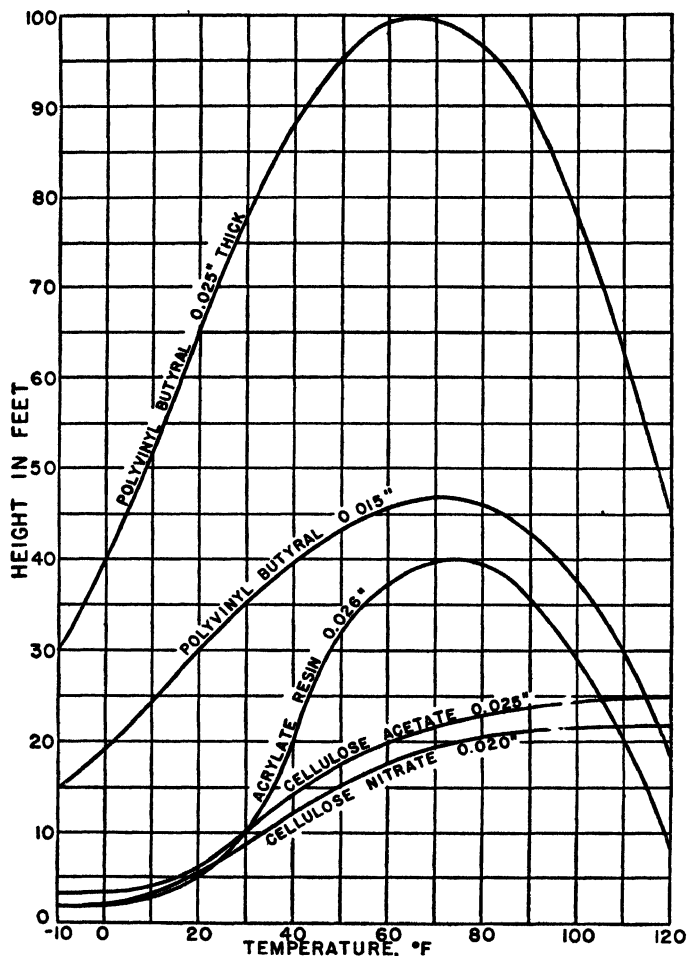


Figure 157. Temperature vs. resistance to break for safety glass constructed with different commercial types of plastic interlayer. (Break-through of one-half pound steel ball dropped upon a 12 × 12 inch glass plate supported around its periphery.) (Adapted in part from Sherts and Fix⁸⁶)

tinuous tabs which can be flexed inward or outward, quite independently of each other. This construction has provided ideal strength in a mounting which is resistant to shear and hermetically sealed. The construction of these varieties of "Flexseal" is shown in Figure 158.

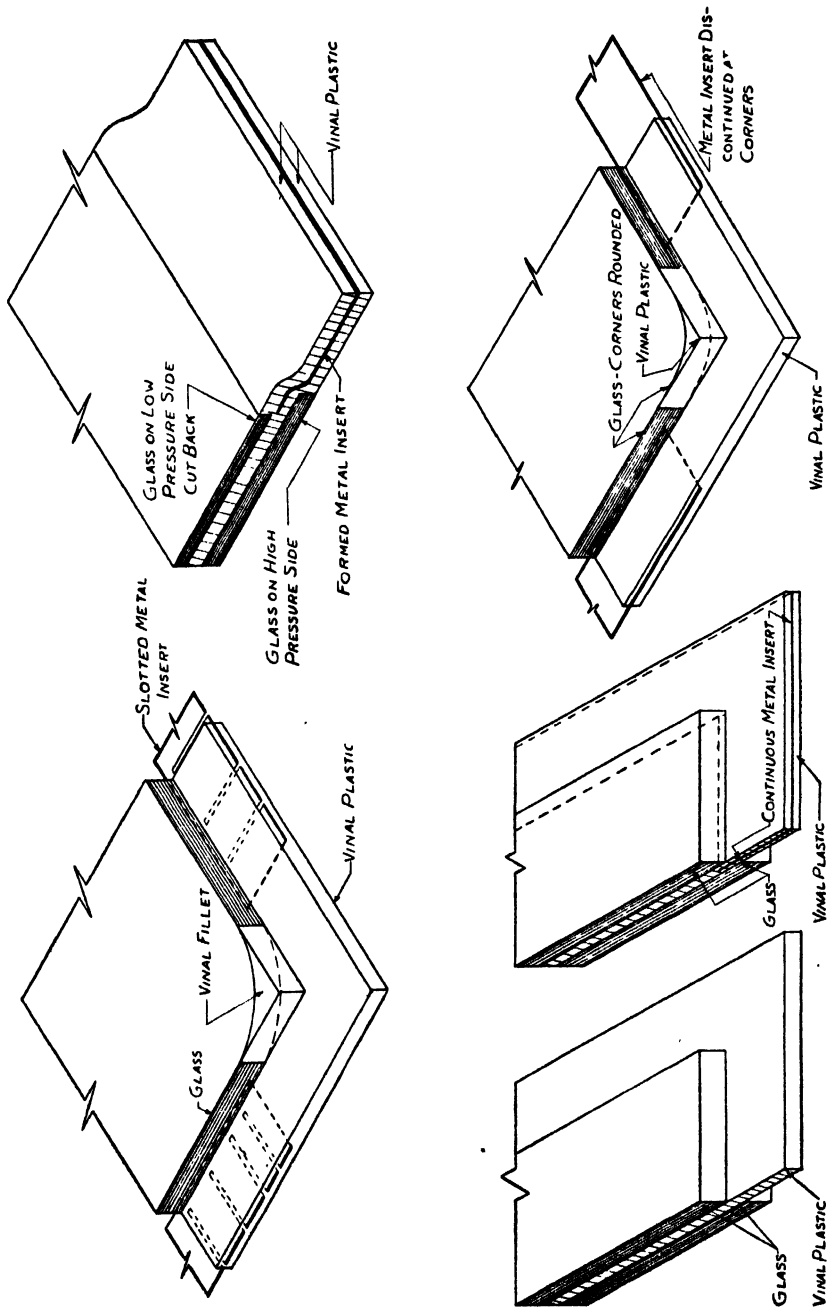


Figure 158. Various constructions of "Flexseal."

Courtesy Pittsburgh Plate Glass Co.

Other kinds of "Flexseal" resistant to tensile as well as shear strains have also been evolved.

Another development of great military significance in the field of aircraft enclosures has been the introduction of laminates consisting of two sheets of polymethyl methacrylate united by means of a polyvinyl butyral interlayer. This assembly yields bird-resisting characteristics, a matter of prime importance in bombers and other military craft. While the relative thickness of methacrylate sheets and butyral sheeting can obviously be varied over a wide range, that used in heavy bombers may consist of 0.150 inch methacrylate sheets laminated with 0.200 inch polyvinyl butyral interlayer.

In contrast to glass laminates manufactured with vinal sheeting, those made from polymethyl methacrylate sheets require the use of an adhesive. Development of a satisfactory bond proved to be one of the major problems, but it has been solved. The sandwich construction is first built up and united in flat sheet form, then blown or drawn. The adhesive employed must be such as to preclude any crazing which might occur during the forming of such an assembly and must also be free from subsequent blistering upon exposure to tropical heat. The successful solution of these difficult problems, together with the adaptation of the soft vinal plastic edge of "Flexseal" and the discontinuous slotted metal insert to this all-plastic unit, was an outstanding contribution of the Pittsburgh Plate Glass Company to military planes of World War II.

It is interesting to note that the lamination of thick methacrylate sheets to glass by means of polyvinyl butyral sheeting is not feasible because of the fact that, in cooling from the temperature of bonding, the rigid plastic sheet contracts far more than the glass, resulting in marked bending and ultimate breakage of the glass portion of the assembly.

Double-glazed windows are constructed from two panes of glass with an air space between them to reduce condensation where atmospheric conditions differ on the two sides of the glazing. Certain types, especially for aircraft use, are built with polyvinyl butyral resin spacers to separate and seal the edges of the glass sheets, provided with breathers introduced by means of nuts imbedded in polyvinyl butyral inserts.

Polyvinyl butyral resins have also proved useful in other forms. They are available as clear, transparent unplasticized sheets for special packaging requirements where extreme shock resistance is essential as in fishermen's bait boxes, and for other articles exposed to weather. Mechanical properties correspond to those given in Table 60. Such sheets, available under the trade-mark "Vinylite-X" in thicknesses from 0.005 to 0.030 inch and over, can be easily bent and formed by heating.

After automobile manufacture stopped, following Pearl Harbor, and

the demand for safety glass interlayer ceased, polyvinyl butyral was compounded with various fillers and plasticizers and introduced as flexible extruded tubing in place of rubber, where its "dead" character would permit. A few applications were scarcely developed, however, when it was found that this plastic could be used for coating fabric to yield an excellent substitute for rubberized goods. Army raincoats, water bags, life saver jackets, and pontoon bridge floats were a few of the most important military applications to which textiles proofed with polyvinyl butyral resins have been put. The value of these coatings was greatly increased by the development of means of converting the resin to cross-linked "vulcanized" products by admixture with certain phenolic, alkyd, or urea resins, or with other products such as diallyl phthalate or organic isocyanates, followed by heating.

So-called thermosetting or insolubilized grades of polyvinyl butyral are now available from all manufacturers of this resin. Where compounded with pigments and plasticizers and formulated with suitable solvents, they can be applied to cloth with ordinary spreading or calendering machines. Upon evaporation of solvent and heat-treatment at temperatures in the order of 135°, such resinous coatings become tough, resilient, and insoluble in alcohol, acetone, and water.

Low temperature characteristics of insolubilized polyvinyl butyral are poor, the material being stiff even at 0°. At elevated temperatures, its flexibility is comparable to that of plasticized polyvinyl chloride and copolymer vinyl chloride-acetate.

It has already been shown in Figure 144 that abrasion properties of plasticized polyvinyl butyral are much less satisfactory than those of vinyl copolymer resins. Flexibility at low temperature is also much less satisfactory. Unlike copolymer resins, loading of plasticized butyral resins with certain fillers, such as "Calcene," appears to result in reinforcement of strength characteristics, especially insofar as flex fatigue is concerned.

Polyvinyl butyral is also utilized in wood primers and in adhesives for application to wood and other surfaces.

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Chapter 15

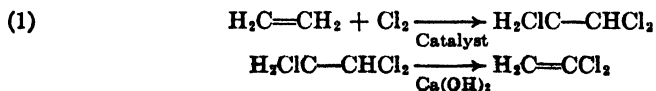
Polyvinylidene Chloride

History

Although its industrial application is recent, monomeric vinylidene chloride, like many chemicals utilized as intermediates in the manufacture of the newer plastics, has been known for years. It was first formed in the laboratory of the French Chemist, Regnault, in 1838. Occasional observations concerning its ability to polymerize were recorded during the first thirty years of this century, but not until the Dow Chemical Company undertook its investigation during the 1930's were the commercial implications of its reactivity surmised. From 1938 onward there has appeared an imposing list of patents relating to the production and utilization of polymers of vinylidene chloride and early in 1940 they were introduced on a commercial scale under the name "Saran."

Chemistry

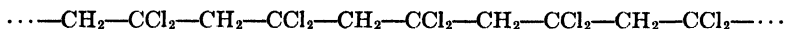
Cracked petroleum gases and brine serve as raw materials for the manufacture of vinylidene chloride. Ethylene is first converted into 1,1,2-trichloroethane by reaction with chlorine at about 60° in the presence of a metalloid or metallic catalyst such as antimony, iron, copper, or manganese. The same intermediate may also be made by addition of chlorine to vinyl chloride. The product is then treated with slaked lime or otherwise dehydro-halogenated, whereupon vinylidene chloride results. The reactions are as follows:



In view of recent achievements attained in the production of such unsaturated halides as allyl chloride by direct high-temperature chlorination of the corresponding olefin, it would appear probable that vinylidene chloride could be obtained under suitable conditions by direct chlorination of ethylene.

The polymerization of vinylidene chloride is readily brought about by

numerous catalysts, especially peroxides. Linear thermoplastic compounds are produced with evolution of approximately 20,000 gram-calories per mole of monomer. A section of a molecule of polyvinylidene chloride can be represented as follows:



From an industrial point of view, however, the most useful polymers are not produced from vinylidene chloride alone. They are rather co-

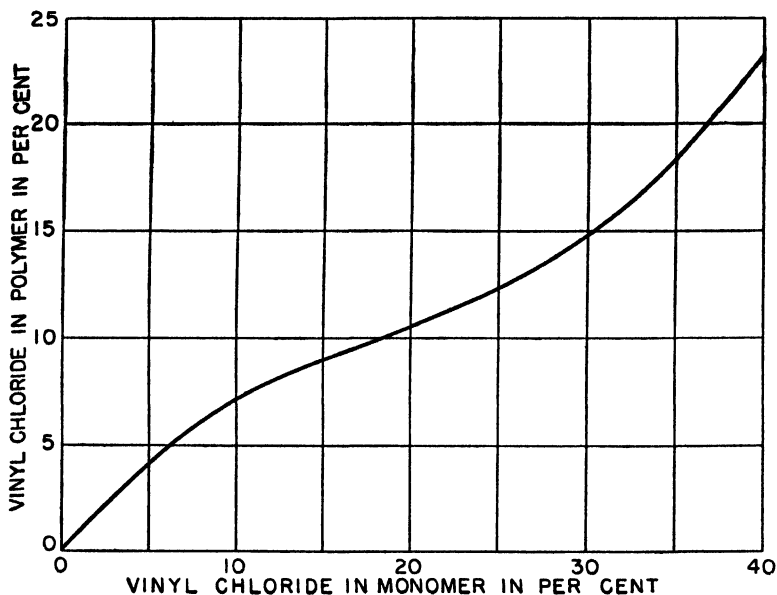


Figure 159. Relation between polymer and monomer composition where vinyl chloride and vinylidene chloride are copolymerized. (Catalyst: 0.50 per cent benzoyl peroxide; temperature: 45°; dark; approximately 50 per cent polymerization.) Since the polymer contains more vinylidene chloride than the monomer, the vinyl chloride concentration in the monomer increases as polymerization progresses; consequently, the product of such a polymerization contains a wide distribution of copolymer compositions in addition to the distribution of chain lengths. (*Reinhardt*⁸¹)

polymers of vinylidene chloride with other unsaturated compounds among which the most interesting is vinyl chloride. By suitable selection of the chemical nature and ratio of monomers and by control of the conditions of polymerization, it is possible to obtain a wide variety of copolymers based on vinylidene chloride as the essential unit structure.

The original ratio of monomers does not remain constant during copolymerization of vinylidene chloride and vinyl chloride. This fact is illustrated by Figure 159. If, for example, these two compounds are

initially present in the ratio of 90 to 10 respectively, after reaction has proceeded to the extent of 80–90 per cent completion, the corresponding ratio of monomer units in the final polymer is in the order of 95 to 5.

Moreover, the rate of copolymerization, as shown by Figure 160, is usually less than the rate of polymerization of either monomer alone.

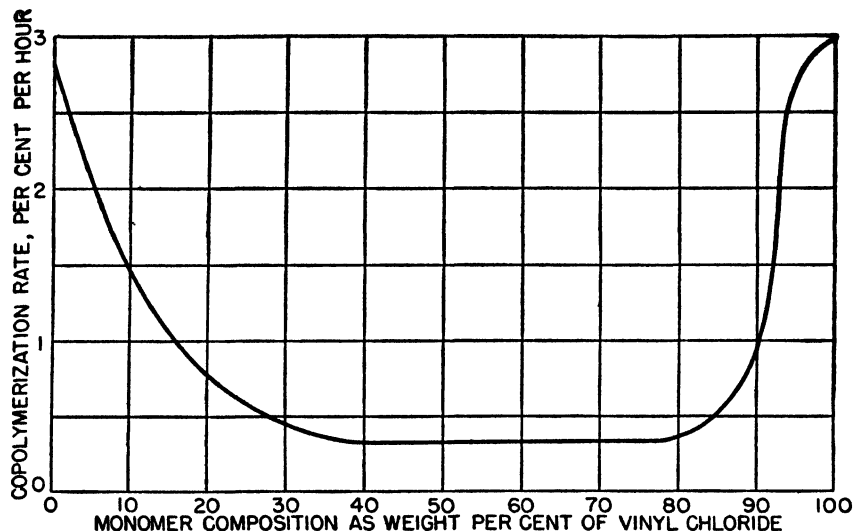


Figure 160. Copolymerization rate of vinylidene chloride and vinyl chloride as a function of monomer composition. (Catalyst: 0.50 per cent benzoyl peroxide; temperature: 45°; dark.) (Reinhardt³¹)

The relationships between rate of copolymerization, temperature, and catalyst concentration are brought out in Figure 161.

Softening points of copolymers ranging from 70° to over 180° can be obtained. The softening range of polyvinylidene chloride itself is 185–200°. Consistency may be varied from soft, flexible products to hard and rigid materials. Those commercial products which are at present available under the name "Saran" are copolymers of vinylidene chloride and vinyl chloride containing at least 85 per cent of the former; within the limits of 85 and 100 per cent of vinylidene chloride, insolubility in organic liquids and resistance to chemical attack remain practically constant. They are reported to possess molecular weights in the order of 20,000. Their softening points range between 120 and 140°. Goodrich's "Geon" 200 series of resins comprise vinyl chloride in preponderance.

Decomposition of polymers and copolymers of vinylidene chloride, with evolution of hydrogen chloride, is catalyzed by iron and copper at temperatures above 130°.

Polyvinylidene chloride shows a greater degree of crystallinity than

most other thermoplastics, although this property is less conspicuous in copolymers than in pure polymers and decreases with decreasing vinylidene chloride content. Both polymers and high vinylidene chloride copolymers possess unusually narrow softening ranges. If heated above this range they become amorphous. If they are then cooled quickly they

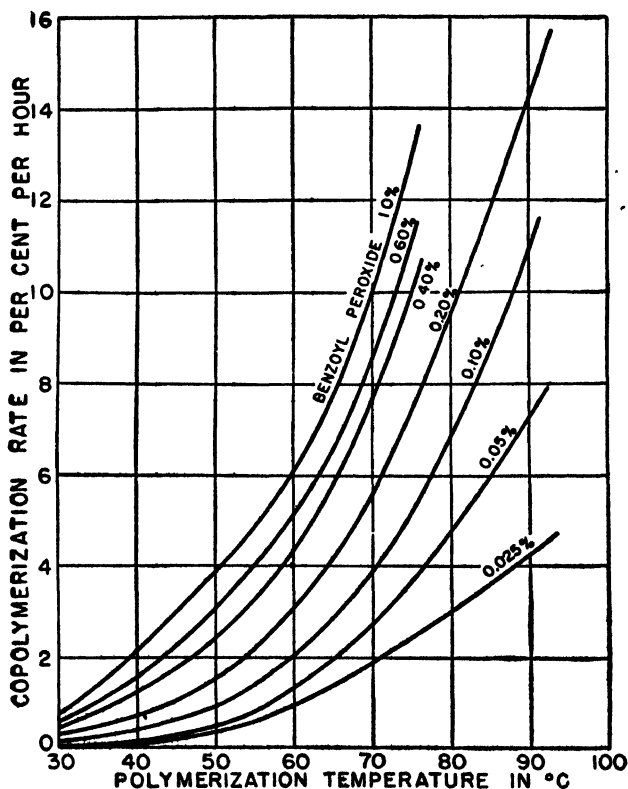


Figure 161. Copolymerization rate of vinylidene chloride and vinyl acetate as a function of polymerization temperature and catalyst concentration. (Monomer composition: 85 per cent vinylidene chloride, 15 per cent vinyl acetate; dark.) (Reinhardt²¹)

remain in the amorphous state, which, on standing at room temperature, gradually changes to a pseudo-crystalline condition. The rate of this crystallization depends on the temperature and on whether or not the solid polymer is cold worked. The time required for crystallization varies from a few seconds to several weeks. The relations between temperature and induction period before crystallization begins and between temperature and time required for crystallization are shown in

Figures 162 and 163. While the crystalline character of polyvinylidene chloride is not sufficiently well developed to be visible to the naked eye or even under the microscope, yet it is apparent from the x-ray diffraction pattern. Figure 164 shows the x-ray pattern for amorphous "Saran" which

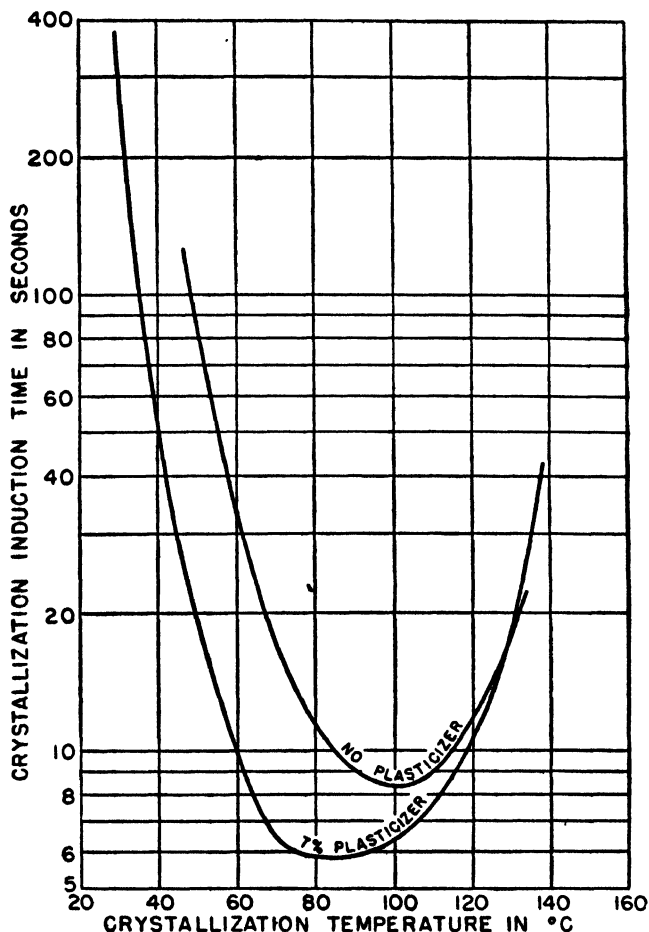


Figure 162. Typical crystallization induction period curves for a normally crystalline vinylidene chloride-vinyl chloride copolymer. (Specimen thickness: 0.050 inch.) (Reinhardt³¹)

is in marked contrast to the ring-like diffraction pattern of Figure 165, characteristic of the crystalline state. By suitable mechanical working such as cold-stretching, the amorphous material can be converted into an oriented crystalline state which gives rise to the lattice x-ray diffraction pattern of Figure 166.

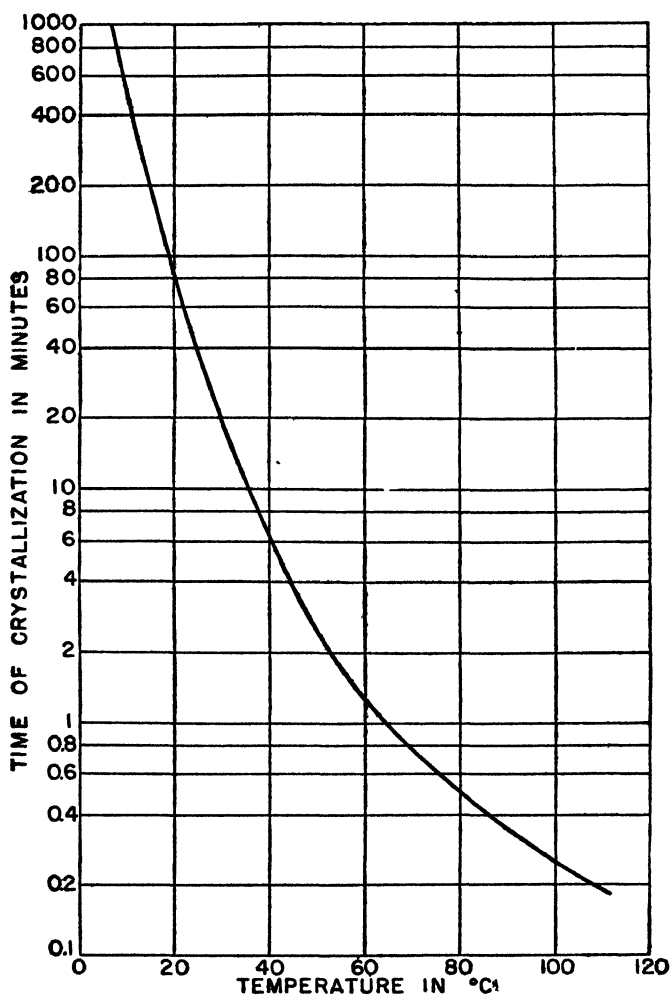


Figure 163. Recrystallization time of "Saran" versus temperature. (*Goggin and Lowry*¹⁸)



Figure 164. X-ray diffraction pattern of amorphous "Saran."

Courtesy The Dow Chemical Co.

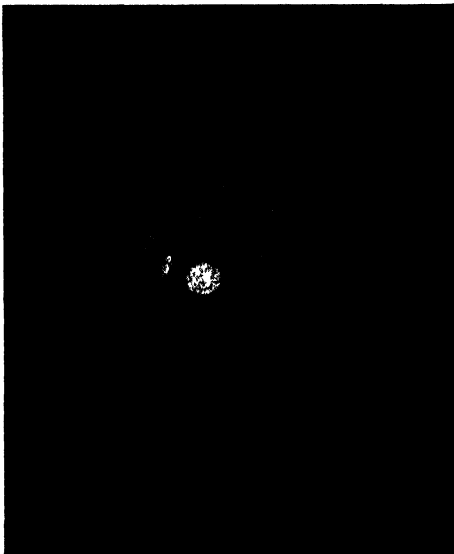


Figure 165. X-ray diffraction pattern of crystalline "Saran."

Courtesy The Dow Chemical Co.

The line of demarcation between crystalline and amorphous states of polyvinylidene chloride in a single segment of extruded and properly worked material is clearly visible under polarized light, as shown in Figure 167.

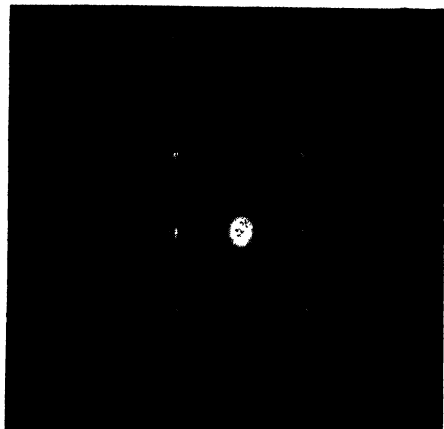
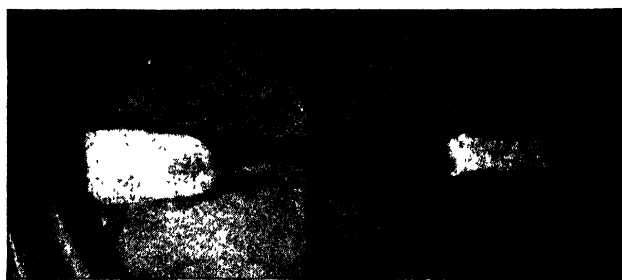


Figure 166. X-ray diffraction pattern of oriented crystalline "Saran."

Courtesy The Dow Chemical Co.



unoriented
crystalline

amorphous

oriented
crystalline

Courtesy The Dow Chemical Co.

Figure 167. Cross-"Polaroid" picture of physical states of "Saran."

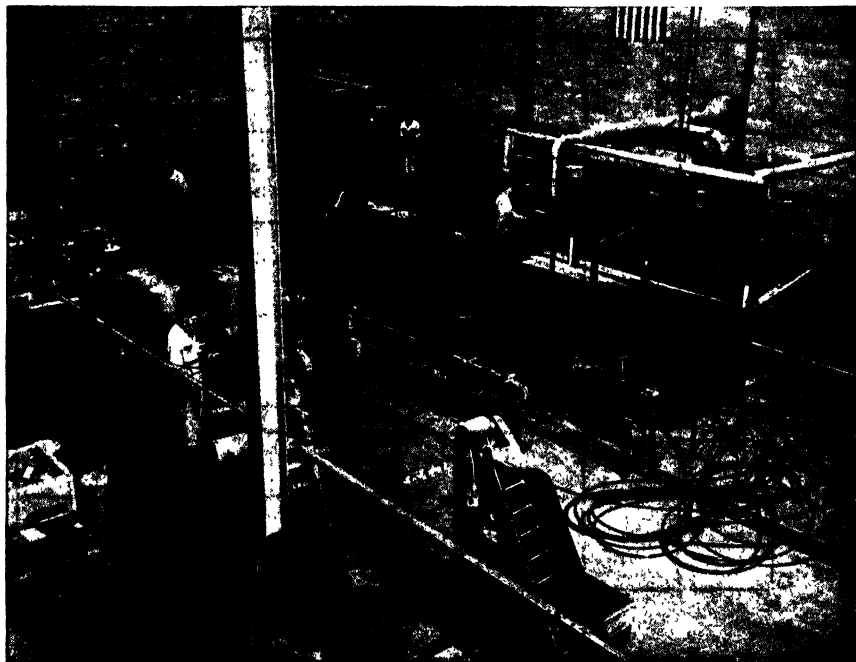
Extruded Shapes

Manufacture. The most important current applications of polyvinylene chloride are in extruded forms. Either powder or granules may be fed into the hopper of a screw-type extrusion machine. The former is favored inasmuch as a milling operation is thus avoided and the bulk factor is of little importance. The powder consists of polymer, plasticizer, and coloring pigments which have been thoroughly admixed in a ball mill.

Because of the fact that the thermal decomposition of Saran is catalyzed

by iron and copper, it is essential to select the materials of construction of the extrusion machine so that neither these metals nor their alloys will contact the plastic at points where the temperature is above 130° . Magnesium alloys, nickel, Z nickel, Hastelloy B, Stellite 10, and impervious nickel plate are recommended.

Satisfactory extrusion of "Saran" can be carried out only in the amorphous state. If heated above its softening range, it acquires a con-



Courtesy The Dow Chemical Co.

Figure 168. A corner of the Dow "Saran" Development Laboratory. In this laboratory studies have been made of the production of "Saran" pipe, tubing, and cordage.

siderable degree of fluidity and can be readily extruded without retention of elastic memory. The extruded product, on cooling, is still largely amorphous. It slowly undergoes recrystallization which is accompanied by marked increase in strength and hardness and a slight increase in density. Controlled heat treatment to bring about recrystallization is often carried out on extruded "Saran."

Where extruded shapes are sufficiently simple and small in cross-section, especially in the case of monofilaments, it is possible to effect a certain degree of orientation. Tensile strength can thus be greatly increased beyond that shown by unoriented, recrystallized "Saran." Orientation is

usually brought about by cold-stretching, preferably at room temperature. This mechanical working simultaneously crystallizes and orients the plastic, although heat-treatment may be resorted to in order to facilitate crystallization.

The relationship between extent of stretching and increase of tensile strength of "Saran" monofilaments is shown in Figure 169.

While the greatest increase in strength characteristics of extruded polyvinylidene chloride is brought about by unidirectional cold-stretching

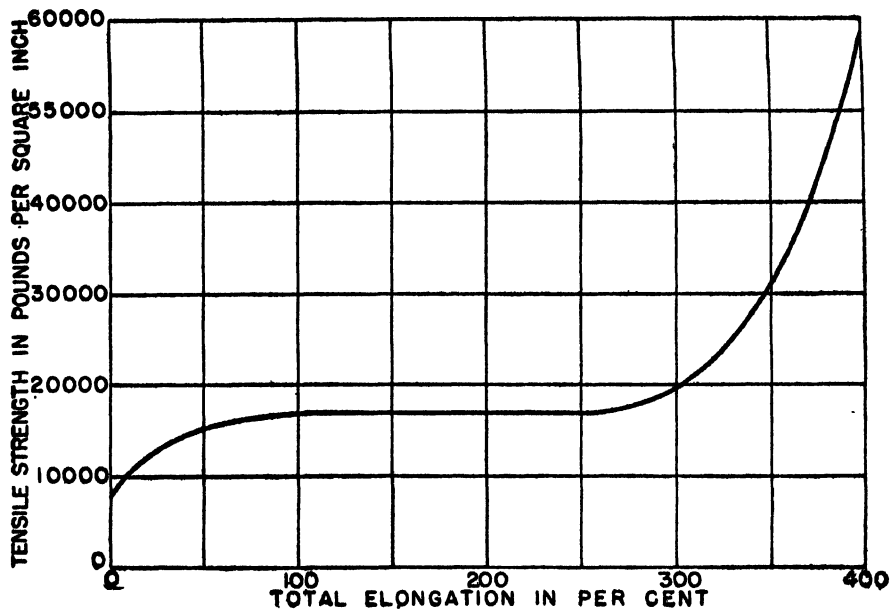


Figure 169. Tensile strength of "Saran" monofilaments versus elongation. (Stretching time: 5 minutes.) (Goggin and Lowry¹⁸)

of monofilaments, control of transverse properties can also be effected for certain shapes by such operations as calendering of tapes, rolling of tubes into oval shapes, blowing of closed forms, and multi-directional stretching of sheet material.

Properties. The most outstanding property of polyvinylidene chloride is its resistance to acids and organic solvents. Except for strong sulfuric acid in which it discolors, "Saran" is affected by neither dilute nor concentrated acids. It is resistant to dilute alkalis. It is discolored by strong caustic and attacked by concentrated ammonium hydroxide. It is highly resistant to water absorption at room temperature. It is unattacked by most organic solvents; important exceptions are ethers like ethyl ether and dioxane, certain chlorinated solvents like ethylene dichloride, and

ethyl gasoline. The resistance of "Saran" to various chemicals at room temperature is shown in Table 62.

Table 62. Chemical Resistance of "Saran" at Room Temperature after Three Months of Continuous Exposure ¹³

Reagent	Stability Rating *
98% H ₂ SO ₄	Good
60% H ₂ SO ₄	Excellent
30% H ₂ SO ₄	Excellent
10% H ₂ SO ₄	Excellent
35% HCl	Excellent
10% HCl	Excellent
65% HNO ₃	Excellent
10% HNO ₃	Excellent
Glacial acetic acid	Excellent
10% Acetic acid	Excellent
5% H ₂ SO ₃	Excellent
Oleic acid	Excellent
50% NaOH	Fair
10% NaOH	Good
28% NH ₃ (aqueous)	Unsuitable
10% NH ₃ (aqueous)	Poor
Ethyl alcohol	Excellent
Ethyl acetate	Fair
Acetone	Fair
Methyl isobutyl ketone	Fair
Carbon tetrachloride	Good
Ethylene dichloride	Poor
Diethyl ether	Poor
Dioxane	Unsuitable
o-Dichlorobenzene	Fair
Ethyl gasoline	Poor
Turpentine	Excellent
Butyraldehyde	Excellent
Triethanolamine	Excellent
Lubricating oil	Excellent
Linseed oil	Excellent
Bromine water	Unsuitable
Chlorine water	Unsuitable
Bleaching solution	Excellent
10% Duponol	Excellent
10% Zinc hydrosulfite	Excellent
15% CaCl ₂	Excellent
15% FeSO ₄	Good
Water	Excellent
Air	Excellent

* These stability ratings are made on the basis of observations of change in appearance, weight, dimensions, tensile strength and hardness.

Unpigmented "Saran" exhibits a cloudy yellowish-green color. In thin oriented filaments it is transparent, although still slightly yellow. The color can be masked by certain dyes so that other transparent shades are available in the case of extruded filaments and rattan. The natural color

Table 63. Properties of Polyvinylidene Chloride ("Saran")*

Property	Unoriented Forms	Oriented Forms
Extrusion Temperature	Up to 375° F	Up to 375° F
Injection Molding Temperature	300–400° F	
Injection Molding Pressure	10,000–30,000 lbs/in ²	
Compression Molding Temperature	250–350° F	
Compression Molding Pressure	500–5,000 lbs/in ²	
Mold Shrinkage (Injection Molded)	0.008–.012 in/in	
Specific Gravity	1.68–1.75	1.68–1.75
Refractive Index n_D	1.60–1.63	1.60–1.63
Tensile Strength, Ultimate ⁽¹⁾	3,000–8,000 lbs/in ²	15,000–40,000 lbs/in ²
Elongation at Yield Point ⁽²⁾	15–25%	20–30%
Modulus of Elasticity, Tension ⁽³⁾	0.7–2.0 × 10 ⁵ lbs/in ²	0.7–2.0 × 10 ⁵ lbs/in ²
Flexural Strength	8,000–15,000 lbs/in ²	Flexible
Compressive Strength at Yield Point	75,000–85,000 lbs/in ²	
Impact Strength, $\frac{1}{2} \times \frac{1}{2}$ " Notched Bar, Izod	2–8 ft lbs/in	
Thermal Conductivity	2.2×10^{-4} cal/sec/cm ² /° C/cm	2.2×10^{-4} cal/sec/cm ² /° C/cm
Specific Heat	0.32 cal/° C/gm	0.32 cal/° C/gm
Thermal Expansion	15.8×10^{-6} /° C	
Resistance to Heat (Continuous)	170° F, approximately	170° F, approximately
Resistance to Heat (Intermittent) ⁽⁴⁾	212° F	Shrinks above 170° F
Softening Point	240–280° F	240–280° F
Distortion Point	150–180° F	
Volume Resistivity (50% Relative Humidity and 25°)	10 ¹⁴ –10 ¹⁶ ohm-cms	
Breakdown Voltage, 60 Cycles, instantaneous,		
0.125" thickness	500 volts/mil	
0.020" thickness	1500 volts/mil	
0.001" thickness	3000 volts/mil	
Dielectric Constant 60, 10 ³ and 10 ⁶ Cycles	3–5	3–5
Power Factor 60, 10 ³ and 10 ⁶ Cycles	0.03–.15	0.03–.15
Water Absorption, ASTM, D570–40T	Less than 0.1%	Less than 0.1%
Burning Rate	Self Extinguishing	Self Extinguishing
Effect of Age	None	None
Effect of Sunlight	Darkens Slightly	Darkens Slightly
Effect of Acids, Alkalies, Solvents	None to Slight	None, Slight
Effect of Metal Inserts	Inert	
Machining Qualities	Good	
Welding Ability	Unexcelled	
Clarity	Translucent to Opaque	Translucent to Opaque
Color Possibilities	Extensive	Extensive
Hardness:		
Rockwell Superficial	15Y, 65–95	
Durometer A	Above 95	
Rockwell M	50–65	

⁽¹⁾ The tensile strength as shown here covers a wide range in size and degree of orientation of the stretched products.

⁽²⁾ Ultimate elongation is greater than that shown here, but it is generally less significant.

⁽³⁾ The modulus of elasticity figures listed here were computed from the stress-strain curve below the yield point.

⁽⁴⁾ Oriented monofilaments retain more than 50% of their room temperature strength at 212° F, but unless restrained, they tend to shrink at temperatures of 170° F or above.

* Manufacturers' data. The Dow Chemical Company.

can, of course, be covered in a variety of opaque grades by suitable pigmentation.

Polyvinylidene chloride is nonflammable, non-toxic, tasteless, and odorless of itself, although, by reason of its plasticizer content, a sweetish odor may be detected on heating or machining molded or extruded shapes.

Like other thermoplastics, polyvinylidene chloride decreases in strength with increasing temperature. Oriented monofilaments fabricated into 0.027 inch diameter cordage, for example, show a breaking strength of 15,000 lbs per sq in at 120° as compared with over 40,000 lbs per sq in at room temperature. Safe working pressures for "Saran" tubing, in terms of temperature, are discussed on page 404.

The physical properties of "Saran" can be varied widely by mechanical working. General characteristics of both oriented and unoriented forms are listed in Table 63.

Applications. Although polyvinylidene chloride is a newcomer among plastics, it has already found important applications in many fields. Extruded rod is utilized in the fabrication of gaskets and valve seats. Extruded tubing is produced in diameters up to $\frac{3}{4}$ inch o.d., with wall thickness ranging from 0.015 to 0.062 inch. It has been extensively used in defense housing projects in place of copper. It has found use in control devices handling fluids at temperatures below 170°F, in lubricating oil and brine transfer systems, in chemical equipment, and electrical conduits. Refrigeration and air conditioning equipment have proved to be important outlets for "Saran" tubing. Although "Freon" can be handled by "Saran" at moderate temperatures, certain refrigerants, especially those which are chlorinated solvents, will affect it. Care must therefore be exercised and tests applied in each specific case.

Bursting pressures of "Saran" tubing at 25° are listed in Table 64.

Table 64. Bursting Pressures of "Saran" Tubing at 25°¹²

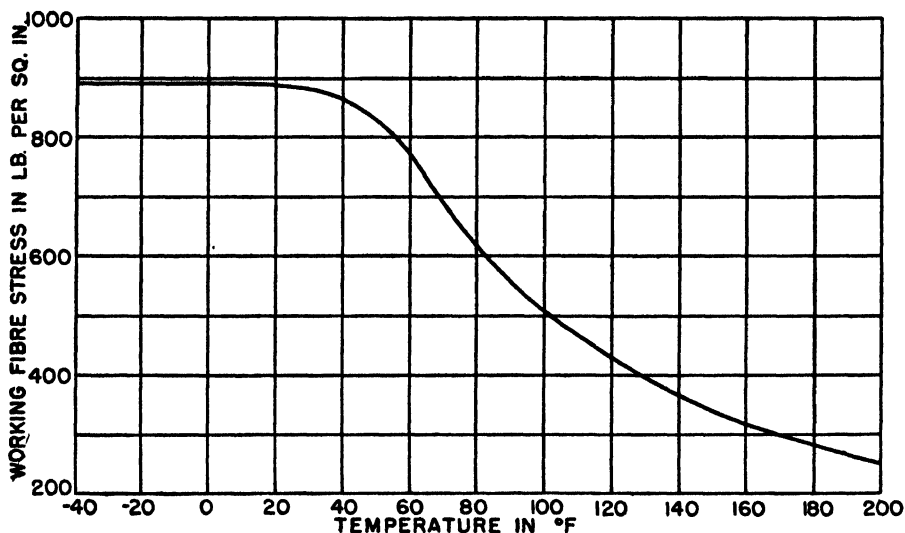
O.D. (in)	Wall (in)	Bursting Pressure (lbs/sq in)	Working Pressure Safety Factor = 5 (lbs/sq in)
$\frac{1}{8}$.031	1900	380
$\frac{3}{16}$.031	1250	250
$\frac{1}{4}$.031	900	180
$\frac{1}{4}$.045	1350	270
$\frac{1}{4}$.062	1900	380
$\frac{5}{16}$.031	700	120
$\frac{5}{16}$.062	1700	340
$\frac{3}{8}$.031	575	115
$\frac{3}{8}$.062	1250	250
$\frac{1}{2}$.045	630	126
$\frac{1}{2}$.062	880	176
$\frac{5}{8}$.045	490	98
$\frac{5}{8}$.062	700	140
$\frac{3}{4}$.045	410	82
$\frac{3}{4}$.062	575	115

The relationship between temperature and working fiber stress of Saran tubing is given in Figure 170. By using the formula:

$$\text{Working fiber stress} = \text{Working pressure} \times \frac{(\text{o.d.})^2 + (\text{i.d.})^2}{(\text{o.d.})^2 - (\text{i.d.})^2}$$

where o.d. and i.d. are outside and inside diameters, the safe working pressure for tubing of any given dimensions can be readily calculated.

Black "Saran" pipe is available in sizes from $\frac{1}{2}$ inch to 5 inches, I.P.S.,



Courtesy The Dow Chemical Co.¹²

Figure 170. Working fiber stress for "Saran" tubing versus temperature. Assumed safety factor, 5.

and is utilized not only in general plumbing installations, but especially in chemical conduits and in other locations where corrosion-resistance is of prime importance. Bursting pressures for pipe of various sizes are given in Table 65.

Table 65. Bursting Pressures of "Saran" Pipe¹³

Nominal Size	O.D.	I.D.	Calculated Bulk		Bursting Pressure at 25° C	Working Pressure
(in)	(in)	(in)	(lbs/ft)	(ft/lb)	(psi)	(psi)
$\frac{1}{2}$.840	.546	.236	4.23	1300	260
$\frac{3}{4}$	1.050	.742	.320	3.12	1060	210
1	1.315	.957	.475	2.12	970	190
$1\frac{1}{4}$	1.660	1.278	.650	1.550	820	160
$1\frac{1}{2}$	1.900	1.500	.790	1.270	740	150
2	2.375	1.939	1.090	.920	620	125
$2\frac{1}{2}$	2.875	2.277	1.805	.554	570	115
3	3.500	2.842	2.480	.403	510	105
$3\frac{1}{2}$	4.000	3.307	3.010	.332	470	95
4	4.500	3.749	3.760	.266	460	90

Molded couplings are available for both tubing and pipe. Tubing can be readily flanged with heated tools. Pipe can be threaded with standard plumbers' tools, either hand or power driven, although it may sometimes be found desirable to reinforce the center with a wooden plug while tapping in order to prevent the flexible plastic from partially collapsing under the die, thus giving rise to an incomplete thread. "Saran" pipe can,



Courtesy The Dow Chemical Co.

Figure. 171. Welding "Saran" sheet around a chemical agitator by friction. A high speed rotating tool creates enough frictional heat between the "Saran" rod and the sheet being welded to lay down a heavy bead.

moreover, be butt-welded on the spot by softening the ends with heat and rapidly joining them. The joint is as strong as the rest of the pipe.

"Saran" pipe and tubing are recrystallized, but not oriented. Extruded and cold-stretched plastic, used in artificial rattan, is superior to the natural product in its ease of cleaning, its resistance to soap and other cleaning fluids, its resistance to perspiration, and its availability in a wide range of colors.

Cold-stretched Saran monofilament, in diameters of 0.007 to 0.100 inch,

is utilized in woven textiles for automobile and airplane upholstery, in draperies, ladies' shoes, suitcases, fungi-resistant rope, fishing leaders, filter fabrics, and corrosion resistant, partially transparent screening. "Saran" screening has played a major role in the war effort. A large share of Saran production has been extruded into olive drab monofilament for this application. Life tests in the South Pacific have indicated that the product will outlast any metal screening available, and that it is not affected by fungus and will not burn. It has been used extensively in both screen type tent walls of temporary advanced bases and in more permanent housing facilities for officers and enlisted men.

Other extruded shapes include chemical conveyor belts and tape for miscellaneous uses, such as die punching.

Injection Molding and Miscellaneous Uses

Although the most extensive applications of polyvinylidene chloride have thus far been in the field of extruded articles, injection molding is also carried out on a large scale and has been successfully applied to the manufacture of spray gun handles where solvent and abrasion resistance have made it an eminently desirable successor to aluminum. It has also been used in the production of innumerable other articles such as valve seats, acid dippers, rayon equipment, couplings for pipe and tubing, and even bugles.

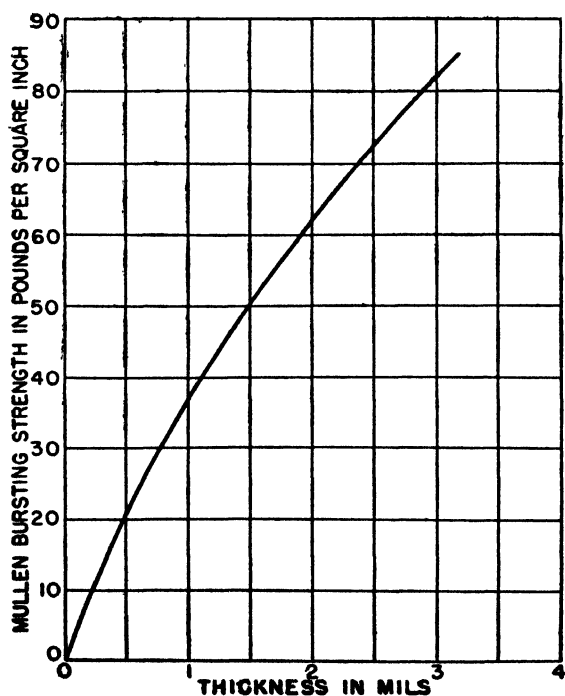
Injection molding machines, like extruders, should be equipped with metals which do not catalyze thermal decomposition at points contacting the plastic above 130°. Molds themselves may be made of the usual types of steel because they operate below this temperature; this, of course, applies only to injection and not to compression molds which have to be heated to molding temperatures. The injection molding of polyvinylidene chloride is unique in that the mold should be maintained at a temperature ranging from 80 to 100° in order to facilitate recrystallization of the plastic article before its removal. "Saran" can be ejected from the hot mold without serious warpage.

Polymeric vinylidene chloride, appropriately plasticized and stabilized, is also available in the form of film, known under the trade name "Saran" film, Type M. It is oriented and therefore strong. It is nonflammable, nearly colorless, and highly flexible. It exhibits extraordinarily low water absorption and water vapor transmissivity—characteristics which are relatively unaffected by repeated folding or creasing. It possesses excellent chemical resistance. Rates of transmissivity of helium, hydrogen, carbon dioxide, oxygen, and nitrogen range from not more than 0.70 to less than 0.01 l/sq m/24 hrs for 125 gauge film. Initial tear resistance is excellent, but—in common with other plastic membranes—it is low



Figure 172. Packing of a precision instrument in Saran film. This moisture barrier is used in conjunction with silica gel and will prevent rusting of precision parts.

Courtesy The Dow Chemical Co.



Courtesy The Dow Chemical Co.¹⁴

Figure 173. Bursting strength of Saran film, Type M, at 77° F. versus thickness.

once a tear has been started. "Saran" film is produced in thicknesses of 0.001 inch upwards. Principal uses thus far have been for packaging metal parts, especially in military applications. Skin-tight coverings can be produced by exposing loosely wrapped packages to temperatures sufficiently high to induce loss of orientation. At 85 to 95° F such shrinkage becomes apparent. Above 160° F, unrestrained shrinkage occurs in a few seconds. Odorless and tasteless film for food packaging is under development. Properties of "Saran" film are given in Table 66. Figure 173 shows the relation between bursting strength and thickness of "Saran" film.

Table 66. Properties of "Saran" Film—Type M ¹⁴

(All data referred to are averages for 0.002" film at 77° F and 50% relative humidity.)

General	
Specific Gravity	1.68
Specific Volume—cubic inches/pound	16
Area Factor—square inches/pound	7000
Moisture Vapor Transmission—grams/100 inches ² /24 hours at 100° F and 90% Relative Humidity Differential	0.14
Water Absorption—1 week at 77° F	0.02%
Thermal	
Softening Point	240–260° F
Burning Rate—A.S.T.M. D568–40	Self-Extinguishing
Specific Heat—cal/° C/gram	0.32
Thermal Conductivity—cal/sec/cm ² /° C/cm	2.2×10^{-4}
Resistance to Heat—up to 125° F continuous	Excellent
Resistance to Heat—up to 170° F intermittent	Good
Resistance to Cold—tested to – 40° F	Good
Mechanical	
Tensile Strength—pounds/inch ²	7–11,000
Elongation—per cent	25–35
Bursting Strength—pounds/inch ²	67
Tear Strength—grams-Elmendorf	40
Drop Impact—(1" steel ball)—feet—	
77° F	10
32° F	> 7½
0° F	> 7½
Optical	
Refractive Index	1.61
Transmission of White Light	90%
Ultraviolet Cut-Off	3500Å
Transmission of Infra-Red	90%
Electrical	
Dielectric Constant	
1,000 cycles	2–4
1,000,000 cycles	2–4
Power Factor	
1,000 cycles	10–13
1,000,000 cycles	3–5
Dielectric Strength, volts/mil.	5000

As with some other thermoplastic films and fabrics, it is possible to heat-seal "Saran" glm. This operation can be carried out, if desired, by electronic heating.

Polyvinylidene chloride has been developed as a binder-modifier for abrasive particles in grinding wheels.

The use of Saran as a webbing agent in "Vinylite" coatings destined for use as a sprayable packaging material for protecting heavy military equipment in storage has been mentioned in Chapter 14.

Among "Geon" resins, announced by Goodrich in 1944, members of the 200 series are copolymers of vinyl chloride and vinylidene chloride. These products may be dissolved in methyl ethyl ketone and plasticized with dioctyl phthalate. They are recommended for molding, extruding, calendering, solution coating, impregnating, and film casting.

During the war, a vinylidene chloride copolymer with vinyl chloride in approximately 1:1 ratio was developed. Although future manufacture of this product is not contemplated it is interesting to note that by suitable treatment it can be cross-linked or "vulcanized." This operation can be carried out by heating with a rubber accelerator and zinc oxide.

Trade Names and Prices

Polyvinylidene chloride is manufactured by the Dow Chemical Company under the name "Saran." Several fabricators have been licensed to extrude it and carry out injection molding. A few of these licensees have re-named their products with their own trade-marks, among which are "Mills Plastic," "Permalon," "Vec," and "Velon."

In 1943, "Saran" extrusion powder averaged 0.54 dollars per pound. Tubing of $\frac{3}{8}$ inch outside diameter and 0.031 inch wall thickness was priced, subject to discounts, at \$9.60 in hundred foot lengths, with cost ranging downward to \$4.80 per hundred feet in lots of 10,000 feet or more. List prices of pipe, subject to discount, ran from 68 cents to \$2.64 per foot in sizes from $\frac{1}{2}$ inch to 2 inches for lots of 1000 feet or more.

The "Geon" 200 series of resins has been mentioned in the preceding section.

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Chapter 16

Polystyrene

History

Although polystyrene is a relatively new commercial plastic, it has been known to science for over a hundred years. Styrene, itself, was first produced in 1831 by distillation of storax obtained from *Liquidambar orientalis*, a tree native to Asia Minor and belonging to the same genus as the North American sweet gum (*Liquidambar styraciflua*). Eight years later, a Berlin apothecary, Eduard Simon, made a further study of styrene and, by heating, obtained from it a solid material which he thought to be an oxide, but which was, in fact, polystyrene.

The polymeric nature of this material was first clearly recognized by A. W. Hofmann and his co-worker, John Blyth, in England in 1845. Not until fifty-five years later, however, was any interest shown in possible commercial applications of polystyrene and another eleven years elapsed before the first significant patents in this field were applied for by the British chemist, F. E. Matthews, who quite logically was also a pioneer in the development of synthetic rubbers made by polymerization of butadiene and its homologues. In English Patent No. 16,278 of 1911, he described both catalytic and thermal polymerization of styrene to yield substances suitable for use in the production of articles then made from hard rubber, "Celluloid," glass, and wood. Shaping of the heat-softened polymer was described and its value as an electrical insulator was recognized.

Although scientific studies of polystyrene before and after Matthews, especially those of Staudinger and his co-workers, contributed substantially to our knowledge of the chemistry of high polymers, yet industrial utilization of these resins had to await development of economic methods for the manufacture of styrene itself. Moreover, it was necessary to invent practical ways of preventing polymerization during storage and shipment of the monomer. The latter discovery came first—in 1922—and was the logical outgrowth of systematic researches of two French chemists, Moureu and Dufraise, who studied autocatalytic reactions and their inhibition. It was found that numerous materials, especially

aromatic amines and phenols, are capable of preventing the polymerization of styrene which, without them, normally occurs upon protracted standing at room temperature. This discovery has since become of great practical merit. It now makes possible the distillation, storage, and shipment of large volumes of liquid monomeric styrene as an industrial chemical.

Not until the end of the 1920's were economical methods developed for large-scale manufacture of styrene. This led to the introduction of polystyrene as a commercial plastic in Germany about 1930, under the trade names "Resoglaz" and "Trolitul." Shortly afterward, in 1933, the Naugatuck Chemical Company introduced "Victron," manufactured under a series of patents issued to Ostromislenski. "Victron" was used in dentures for a short time under the trade name "Marvelyn." The styrene used in making it, however, was relatively expensive, being obtained by dehydrohalogenation of monochlorinated ethylbenzenes. The sales price of the polymer ran from \$1.50 to \$2.00 per pound, the product was slightly yellowish in color, molecular weight was low, and "Marvelyn" dentures failed to give satisfaction. "Victron" disappeared from the market after a few years and in 1937 rights to the Naugatuck patents on polystyrene were transferred to the Carbide and Carbon Chemicals Corporation.

Late in that same year, however, domestic polystyrene again appeared upon the market under the trade name "Styron"—this time from the plant of the Dow Chemical Company. Many years before, the great French scientist-statesman, Berthelot, had formed styrene by pyrolysis of ethylbenzene, but only in poor yields. Dow made this process a commercial success and evolved a water-white resin. Shortly after Dow introduced polystyrene, the Monsanto Chemical Company and the Bakelite Corporation began to supply this resin to the trade, their materials being based on either styrene or polystyrene produced by Dow. More recently, the Catalin Corporation announced introduction of polystyrene sold under their trade name "Loalin."

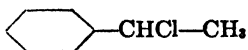
The synthetic rubber program greatly increased the demand for styrene and accelerated its production by several companies, some of whom were already planning manufacture before Pearl Harbor. Concerns now making monomeric styrene include Carbide and Carbon, Dow, Koppers, Monsanto, and, until recently, U. G. I. It is perhaps noteworthy that, in 1940, the last named company began operation of a pilot plant which yielded styrene, along with other unsaturates, by pyrolysis of petroleum oils. Production capacities of various plants are given in Chapter 20. As a by-product of the rubber program, polystyrene has become one of the most common and least expensive ther-

moplastics. Already cellulose acetate has felt the impact of its competition.

Chemistry

Monomeric Styrene. Small percentages of styrene are present in coal tar, but no commercial method has been developed for its recovery as a by-product of coal carbonization. It is also one of the reactive unsaturated materials responsible for the deposition of troublesome gums in gas mains, meters, regulators, and pilot burners handling manufactured gas, especially carbureted water gas. About fifteen years ago it was estimated that 8,000,000 pounds of styrene were available annually from domestic drip oil, but no large-scale recovery has ever been attempted from this source, although U. G. I.'s styrene operation was an outgrowth of this observation.

The first process operated in the United States for the manufacture of styrene was that used by the Naugatuck Chemical Company during "Victron's" brief span of life. Ethyl benzene, obtained by a Friedel-Crafts reaction from ethyl chloride and benzene, was chlorinated in the side chain to a mixture of the two possible monochloroethyl benzenes, largely 1-chloro-1-phenyl ethane,



Hydrogen chloride was subsequently eliminated by reaction with a base.

The styrene thus produced contained traces of chlorine, probably in the ring, from which it could not be freed and the polymer possessed an objectionable light yellow tinge. Although commercial production of the monomer by this process served to arouse American interest in polystyrene, it was far too costly an operation to meet with permanent success and died after a few years.

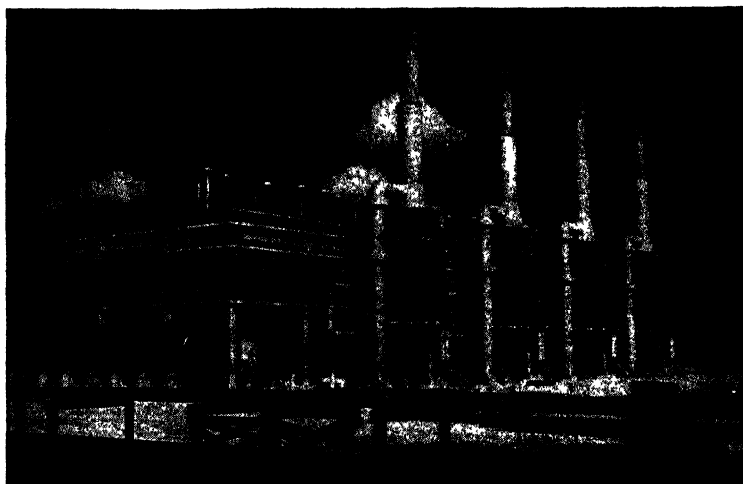
The process employed by the Dow Chemical Company and currently used in various modified forms by several companies, also depends upon ethylbenzene as an intermediate, but resorts to pyrolytic dehydrogenation. Dow's ethylbenzene is produced by liquid-phase reaction of ethylene with benzene in the presence of aluminum chloride at 88° under one atmosphere pressure. Polyethylbenzenes are either disproportionated or recycled, so that high yields of ethylbenzene are obtained. Refinery gases free from other olefins can be used as a source of ethylene for this reaction, provided the ethylene content is at least 38 per cent.

Certain other companies who have entered this field alkylate benzene with ethyl alcohol, using phosphoric acid as catalyst.

Ethylbenzene is catalytically dehydrogenated to styrene at high tem-

peratures, usually between 600 and 800°. Yields of 50 to 80 per cent are reported from the dehydrogenation reaction.

Higher yields of styrene are obtained by cracking isopropylbenzene. Pyrolysis of *t*-butyl benzene, on the other hand, yields largely benzene itself. Isopropylbenzene has become an important constituent of high octane aviation fuel now produced in quantity. It is, therefore, possible



Courtesy The Dow Chemical Co.

Figure 174. One of four ethylbenzene cracking plant blocks of the styrene plant of The Dow Chemical Company at Velasco, Texas. Here ethylbenzene is converted into crude styrene. Original capacity of the plant was 50,000 tons a year, but it will produce 75,000 tons.

that this compound may, in the future, serve as an even more economical source of styrene than does ethylbenzene.

A third method of making styrene has been adopted in a pilot plant formerly operated by Ugyte Sales, a subsidiary of the United Gas Improvement Co. Unlike the other two processes just described, this method does not require ethylbenzene. Clean crude oil is cracked under atmospheric pressure by spraying it onto refractory brick heated to about 1100°. The cracked product is a complex mixture of ethylene, butadiene, isoprene, piperylene, cyclopentadiene, styrene, methylstyrenes, benzene and its homologues, and numerous other unsaturates. Separation and purification, largely by distillation, has been difficult to achieve, but amounts up to 2500 pounds of styrene—2 per cent overall yields based on heavy oil input—have been produced daily in this plant and the material has been used commercially in the manufacture of polystyrene.

Polymerization. Styrene polymerizes slowly upon standing at atmos-

pheric temperature. This reaction can be inhibited by numerous anti-oxidants or polymerization inhibitors containing quinoidal, nitro, amino, nitroso, and phenolic groups. Among such compounds, hydroquinone and *t*-butyl catechol are the most important, being used as commercial stabilizers for shipping and storing monomeric styrene. They can be readily removed by distillation of the styrene over solid caustic.



Courtesy The Dow Chemical Co.

Figure 175. One of The Dow Chemical Company's polystyrene plants, typical of the care exercised in producing ultra-high quality material. This plant is windowless, completely air-conditioned, and also kept under pressure to exclude dirt.

Polymerization of styrene is accelerated by both heat and catalysts. Average chain length of the polymer decreases with increasing temperature and increasing activity of the catalyst selected. Numerous metal and metalloid halides catalyze polymerization, but a trace of oxygen appears to be necessary in order for them to act effectively. Aluminum and stannic chlorides are very active, but the molecular weight of the product is low. Benzoyl peroxide, sold under the trade name, "Lucidol," is more mild and is used commercially. Conditions of polymerization are carefully controlled in order to obtain a product of standard quality and uniformity.

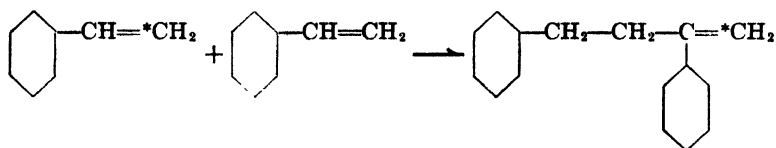
Air must be excluded during polymerization, otherwise yellowing occurs.

The polymerization of styrene is thought to be a chain reaction initiated by activation of the double bonds of a relatively small number of molecules, thus providing nuclei for polymerization which then add inactive molecules with which they come in contact, transmitting their energy of activation to the larger molecules as they grow.

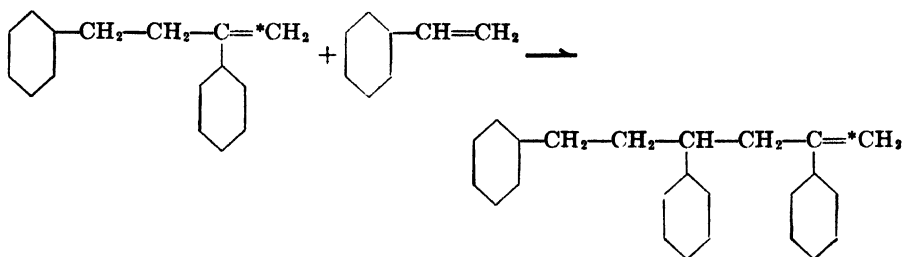
The classification of styrene polymerization as a chain reaction is due in large part to the fact that the average chain length of the polymer

does not increase as reaction progresses. Under a given set of reaction conditions, the length of the polystyrene chains first formed is about the same as the average chain length of those formed at the end of the reaction. Hence, although an appreciable time is required to effect polymerization of a given amount of styrene because of the infrequency of activation and the necessity for activating a sufficiently large number of molecules to use up all of the monomer present in the entire fluid, the chain reaction, once initiated, proceeds with such great rapidity that molecules formed during polymerization, which are intermediate in length between monomer and final polymer have not yet been isolated. As in all cases of polymerization, however, there is, of course, a considerable spread in polymer distribution unless fractionation is carried out.

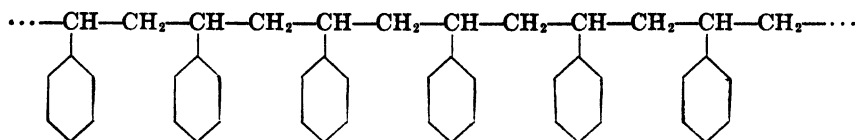
The initial addition of a molecule of styrene to an activated molecule of the same material can be written in the following manner, where the asterisk indicates an activated double bond:



This reaction is again repeated:



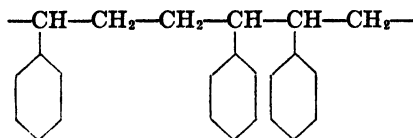
and continues indefinitely, so that the ultimate product is a long linear chain, a portion of which may be represented as follows:



Depending upon the conditions of polymerization, the polymers may vary from hemi-colloids to eucolloids and the degree of polymerization may range between 10 and 5000. A degree of polymerization of 5000 corresponds to a linear chain of 10,000 carbon atoms to which 5000 phenyl radicals are attached, presumably on alternate carbon atoms.

The molecular weight of such a polymer is 520,000. The average molecular weight of commercial grades of polystyrene runs between 18,000 and 200,000. It usually lies in the range of 65,000 to 100,000.

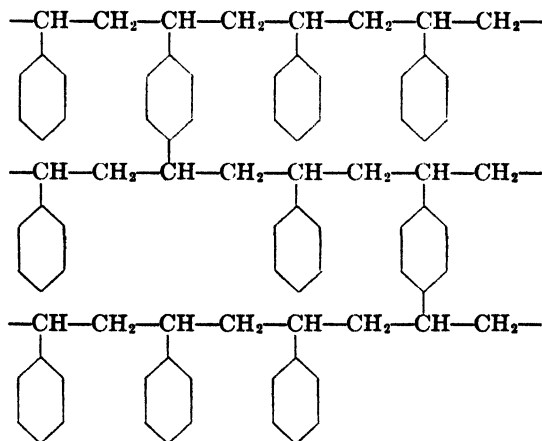
Styrene might polymerize to yield the following unit structure:



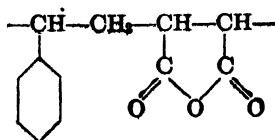
instead of the regularly alternated chain shown above. Neither formula has been indisputably proven. Each has its supporters, but the 1,3 structure is more generally preferred.

Under drastic conditions, the chain of polystyrene may be branched. The properties, especially viscosity characteristics, of the branched chain polymer differ from those of straight chain isomers of similar molecular weights.

Presence of a trace of divinylbenzene in the styrene causes cross-linking of the long chains of polymer, with consequent formation of a tridimensional structure possessing radically different properties, such as increased resistance to heat and solvents. A cross-linked section of such a molecule may be represented as follows:



Certain unsaturated compounds which will not of themselves polymerize, such as maleic anhydride, can be conjointly polymerized together with styrene. The products are known as heteropolymers, differing from copolymers in that the latter are produced by conjoint polymerization of two or more unsaturated compounds each of which can be polymerized alone. The unit structure of a maleic anhydride heteropolymer is as follows:



Properties

Commercial grades of polystyrene are clear, transparent thermoplastics capable of transmitting 90 per cent, or better, of white light. In this property polystyrene resembles the methacrylates.

Long-continued exposure of unstabilized polystyrene to sunlight causes some yellowing. This discoloration is attributable mainly to residual monomer in the polymer. Polystyrene softens slightly above 100° and becomes a viscous fluid at temperatures in the order of 185° . Its A.S.T.M. heat distortion temperature is about 80° . Polystyrene has a thermal transition point at 82° which is essentially a freezing point between a semi-rubbery and solid state. It can be easily molded by injection or extrusion methods and can be dyed in any color by incorporation of various oil-soluble dyes in the monomer prior to polymerization or by grinding or milling a dye or pigment with the polymer.

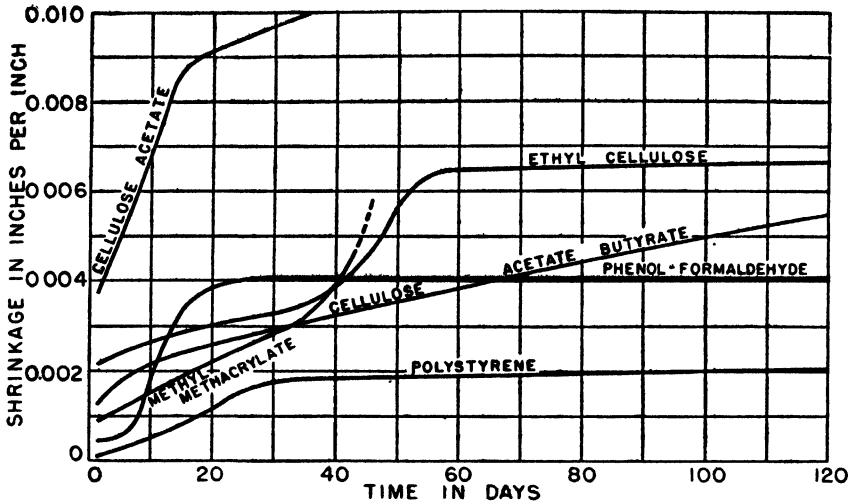
Polystyrene has a density of 1.05. It is one of the lightest plastics.

Although thermoplastic, it possesses unusually good dimensional stability at room and slightly elevated temperatures, being relatively free from cold flow. In this respect it is superior to most other thermoplastics, as shown by Figures 176 and 177.

Polystyrene is an excellent electrical insulator, possessing dielectric properties equal to those of fused quartz. Figure 178 shows the relation of thickness to dielectric strength.

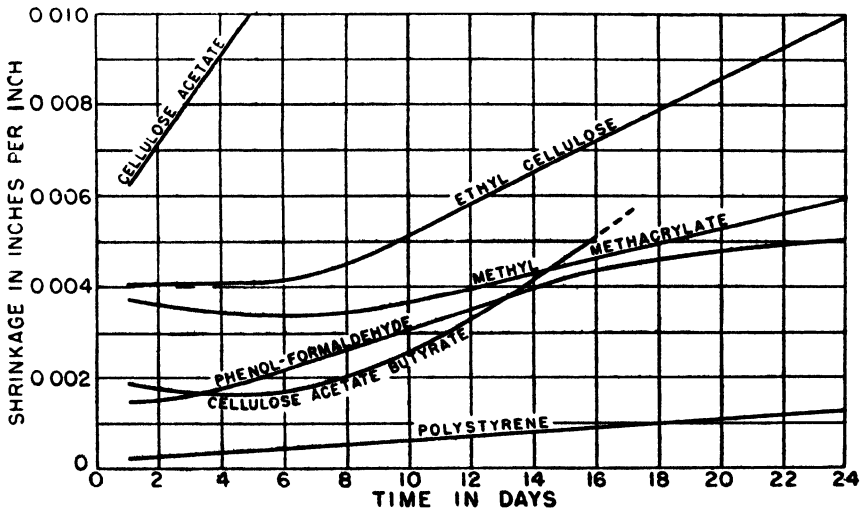
The water resistance of polystyrene is outstanding. Its absorption at room temperature after prolonged standing is nil, and its dimensional changes after such treatment are also nil. Curiously, polystyrene is not impermeable to water vapor, despite its resistance to water absorption. At room temperature and under standard conditions, polystyrene film 5 mm thick transmits approximately 0.5 mg of water vapor per sq cm per hr.

Crazing of polystyrene surfaces has been noted with older types of materials. This phenomenon, exhibited by the appearance of many fine surface cracks, was caused either by too great imposition of strain upon the surface through bending or other form of stressing, or by loss of volatile constituents. Polystyrene currently available is so low in volatile components that crazing no longer results from this source. It can still be caused, however, by excessive stressing of the surface. Articles of polystyrene to be held in place by frames or constrained bases, therefore,



Courtesy The Dow Chemical Co.¹¹

Figure 176. Comparison of the dimensional stability of polystyrene at 50° with typical samples of other plastics. (Length decrease of $1.75 \times 2.50 \times 0.10$ inch samples. Conditioned at 25° and 50 per cent relative humidity before measuring.)



Courtesy The Dow Chemical Co.¹¹

Figure 177. Comparison of the dimensional stability of polystyrene at 70° with typical samples of other plastics. (Length decrease of $1.75 \times 2.50 \times 0.10$ inch samples. Conditioned at 25° and 50 per cent relative humidity before measuring.)

should be mounted with a minimum of stress. In all cases this loading should not exceed a compressive deformation of more than 1 per cent.

Polystyrene is resistant to acids, alkalies, alcohols, and other hydroxylic solvents. It is not dissolved by vegetable oils, fats or waxes. On the other hand, it is readily dissolved by aromatic hydrocarbons, chlorinated

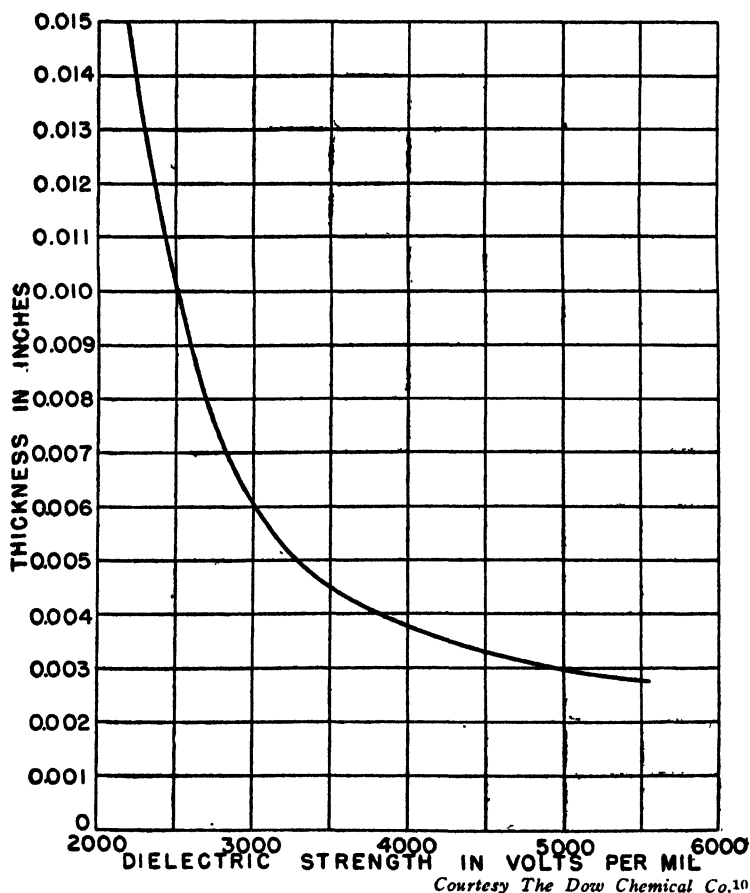


Figure 178. Dielectric strength of polystyrene. ($\frac{1}{4}$ inch electrodes. 25° and 50 per cent relative humidity.)

hydrocarbons, and many esters and ketones. It is swelled, but not dissolved by paraffinic hydrocarbons and acetone.

Impact strength of polystyrene is not appreciably affected by temperatures down to -75° . Indeed, as temperature decreases, injection molded polystyrene gains somewhat in toughness as reflected in shock resistance, tensile strength, elongation, and flexural strength. Hardness also increases with decreasing temperature. This behavior is shown for products

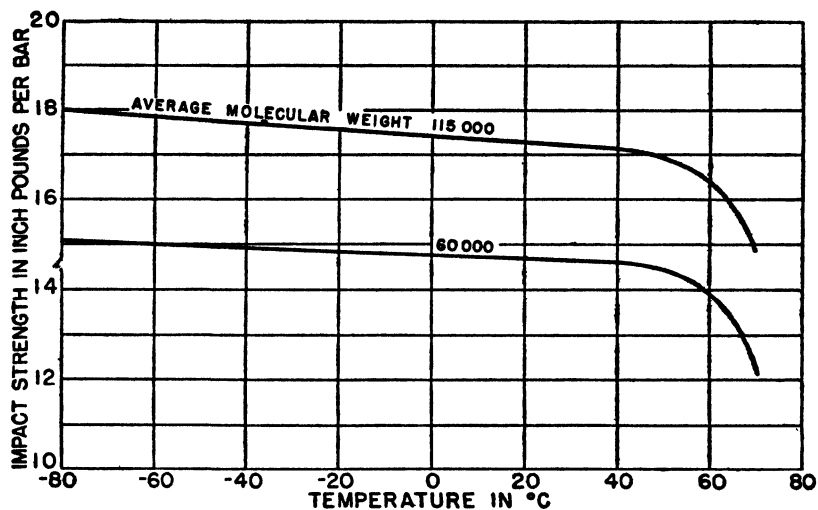


Figure 179. Unnotched Izod impact strength of injection-molded polystyrene. (Carswell, Hayes, and Nason⁸)

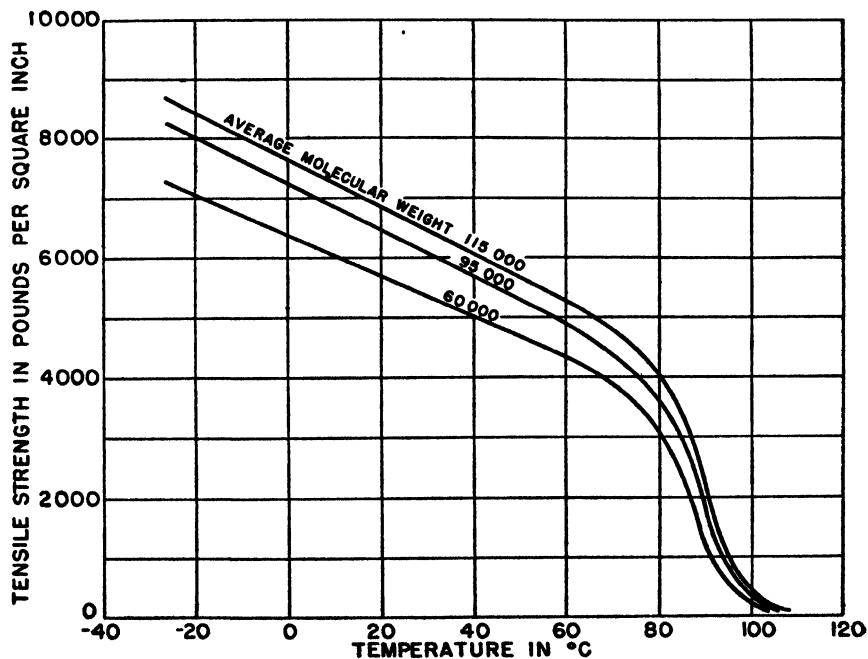


Figure 180. Tensile strength of injection-molded polystyrene vs. temperature. (Carswell, Hayes, and Nason⁸)

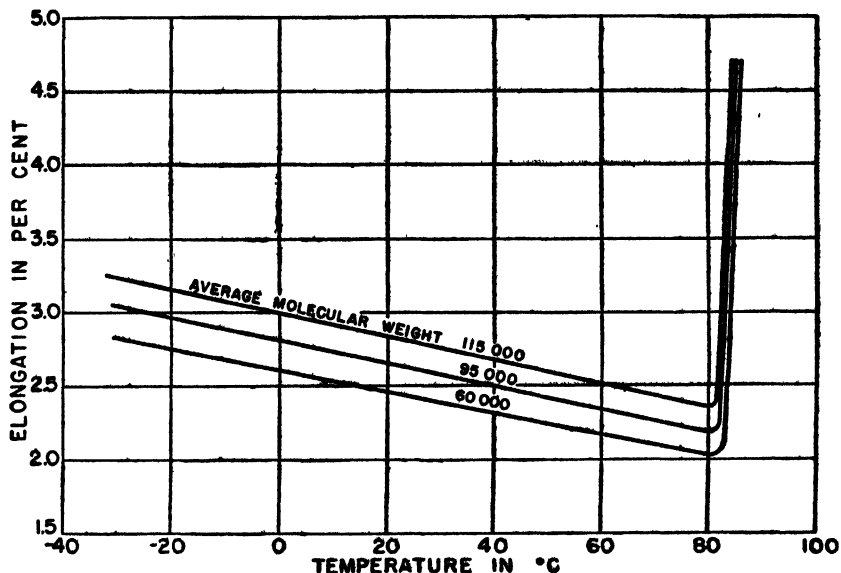


Figure 181. Elongation of injection-molded polystyrene vs. temperature. Elongation at break increases below 80°—an unusual behavior for thermoplastics. (Carswell, Hayes, and Nason⁸)

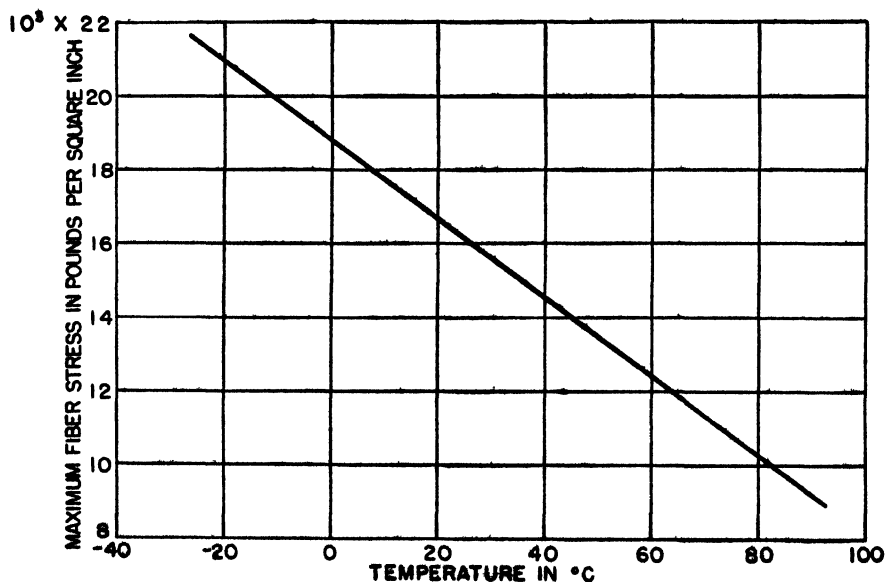


Figure 182. Maximum fiber stress of injection-molded polystyrene vs. temperature. (Average values for M.W. 115,000; 95,000; and 60,000.) (Carswell, Hayes, and Nason⁸)

of different molecular weights in Figures 179 to 183. It has already been noted that polystyrene undergoes a critical transformation at about 82° . Below this temperature, it is a hard, glass-like solid; above, it is relatively soft and more or less rubbery. While certain properties like hardness and heat resistance are substantially independent of molecular

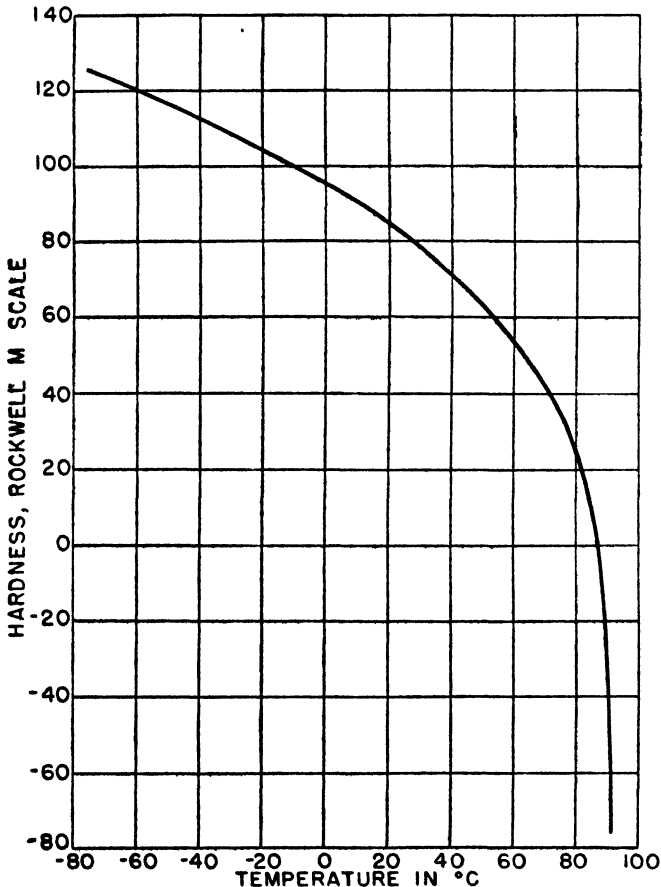


Figure 183. Indentation hardness of injection-molded polystyrene for average molecular weights of 60,000 and 115,000. (Carswell, Hayes, and Nason⁸)

weight, others such as tensile strength, elongation, and impact strength increase therewith.

Polystyrene is unique among plastics in that it gives rise to a somewhat metallic ring when dropped on a hard surface or struck sharply. This property can often be used as a simple test to differentiate it from other plastics.

Unlike hard rubber and the phenolics, polystyrene possesses poor frictional characteristics which are not materially improved by water lubrication. Hence polystyrene cannot be used for under water bearings because of excessive wear.

Physical properties of conventional, high-pressure molded polystyrene are listed in Table 67.

For discussion of the characteristics of low-pressure molded "Polyfibre," see p. 429.

Shapes

Molding Compound. Polystyrene is available in several forms, among which molding compounds rank first in volume and importance. Careful control of polymerizing conditions is exercised during their manufacture so as to ensure uniformity of physical properties and good color. Molding compounds are available in water white and colored grades, both transparent and opaque. Luminescent and phosphorescent pigments provide molded articles capable of glowing in the dark and under ultraviolet light.

Polystyrene can be plasticized with such compounds as dibutyl phthalate and a variety of other high boiling aromatic liquids. Molding compounds as a rule, however, do not contain any plasticizer. Addition of the latter does not affect elongation or toughness advantageously at normal temperatures until rather high concentrations are reached. At the same time, the heat distortion point is lowered so much that plasticized compounds are not suitable for most applications. United States Patents, Nos. 2,289,743-4 and 2,272,996 have been granted on the use of high-boiling aromatic hydrocarbons as plasticizers for polystyrene.

Polystyrene molding powder can be used in compression molding, but this is not recommended except for experimental work. Not only is production slower—universally the case in compression molding of thermoplastics—but polystyrene molding powders require relatively high temperature and pressure and do not flow as well in compression as injection processes.

Customary injection molding temperatures range from 175° to 275°, with pressures of 10,000 to 50,000 pounds per square inch.

The most interesting applications of polystyrene are in electrical parts. Its unusual dielectric properties have guaranteed it a preeminent position in molded television coil forms and insulating parts for both high and low frequency radio. Co-axial beads are molded in large numbers from polystyrene.

Important military applications of polystyrene have utilized its insulating characteristics. Especially spectacular were large, 14 ounce injection

Table 67. Properties of Polystyrene ("Styron")^{10, 11}

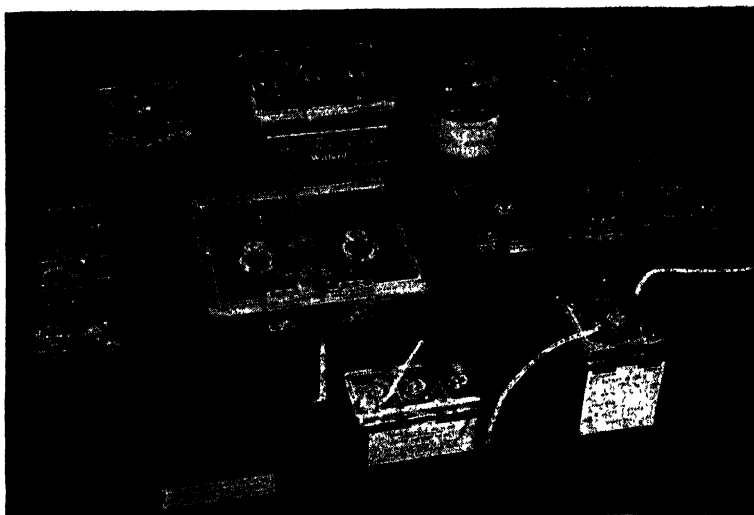
(Determined on Compression Molded Test Pieces)

Molding	
Compression temperature	280–350° F
Compression pressure, lbs/sq in	300–2000
Compression ratio	2.5
Injection temperature	300–500° F
Injection pressure, lbs/sq in	10,000 up
Mold shrinkage, in/in	0.003–0.004
Machining qualities	Good
Buffing or polishing	Fair
Clarity	Crystal clear
Color possibilities	Unlimited
Thermal	
Specific heat, cal/gm/° C	0.324
Thermal expansion coefficient, per ° C	7.0×10^{-5}
Softening point	220–240° F
Distortion temperature ⁽¹⁾	172–176° F
Heat conductivity, cal/sec/cm/° C	3.2×10^{-4}
Mechanical	
Tensile strength, ⁽¹⁾ lbs/sq in	5500–7000
Elongation	1%
Modulus of elasticity, lbs/sq in	$5.5\text{--}7.0 \times 10^6$
Impact strength, ⁽²⁾ 25° to – 70°, ft lbs	0.2–0.3
Hardness:	
Rockwell No. ($\frac{1}{2}$ in ball, 60 kg load)	90–93
Shore Scleroscope No.	83–85
Electrical	
Dielectric strength, volts per mil	See Figure 178
Dielectric constant, 60 cycle	2.6–2.7
1000 cycle	2.6–2.7
1,000,000 cycle	2.6–2.8
Power factor, 60 cycle	0.02 %
1000 cycle	0.02 %
1,000,000 cycle	0.04 %
Resistivity ohm cms	$> 1 \times 10^{15}$
Arc resistance, seconds	240–250
General	
Refractive index at 25°	1.59
Light transmission through 0.1" thickness	90 %
Ultraviolet absorption, complete below	3000 Å
Water absorption ⁽¹⁾ (96 hours immersion)	0.00 %
Specific gravity	1.05
Specific volume, cu in/lb	26.3
Burning rate	Low
Effect of weak acids	None
Effect of strong acids	Discolors
Effect of weak alkalies	None
Effect of strong alkalies	None
Toxicity	Nontoxic

⁽¹⁾ A.S.T.M. D 48–37⁽²⁾ A.S.T.M. D 256–34 T, ft lbs to break Izod notched bar

molded stanchions used to support the radio antenna mast for fast cannon-carrying fighter planes. These stanchions have been subjected to extreme and rapid temperature changes and had to withstand high stresses.

The extraordinary water resistance of polystyrene is applied not only in electrical equipment, but also in such articles as refrigerator parts. Breaker strips, drip trays, freezing compartment doors, and other accessories are produced from this plastic. Resistance to alcohol has led to its application in molded liquor dispensers and accessories. Excellent re-



Courtesy The Dow Chemical Co.

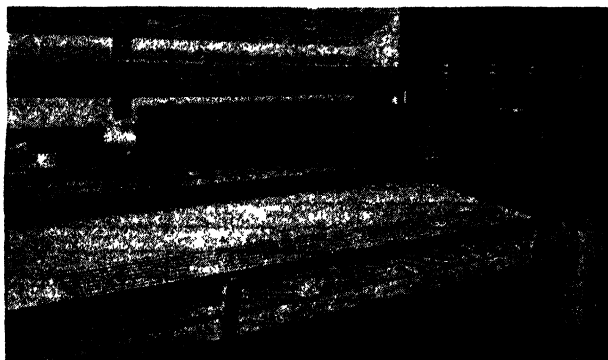
Figure 184. A group of polystyrene batteries designed for special Signal Corps applications.

sistance to acids and alkalies has resulted in its eager acceptance in molded closures for bottles containing these chemicals. In this application, polystyrene screw caps have done away with glass stoppers that were prone to stick and, for safety, required protection with exterior rubber caps. Water and chemical-resistance, dimensional stability, electrical properties, moldability and toughness are factors which led to its adoption in one of its most important wartime applications—*injection molded storage battery cases*.

Numerous housings, frames, and bezels are molded from polystyrene. A refrigerator panel, weighing 19 ounces and having an over-all surface area of 204 square inches, is the largest injection molding to date. It was made of polystyrene. The dimensional stability of this plastic is often an important factor in its selection for applications of this type,

but care should be exercised in mounting, to keep the parts free from strain in order to avoid crazing.

The transparency of polystyrene rivals that of the methacrylates. This characteristic, together with its high index of refraction, is utilized in various light-bending applications, such as edge-lighted instrument dials



Courtesy Plax Corp.

Figure 185. Machine for extruding rod of plastic material such as polystyrene.



Courtesy Plax Corp.

Figure 186. Use of rotating jig to machine unsymmetric pieces of plastic material, such as polystyrene, by routing.

and advertising displays. Advantage is also taken of its clarity in crystals for clocks, gauges, speedometers, and other instruments. Its optical properties have led to application in sparkling molded jewels and ladies' ornaments.

Polystyrene molding powder is available under the trade names of "Bakelite" polystyrene, "Loalin," "Lustron," and "Styron." In carload lots, water clear granules were priced in 1944 at about 25 cents per pound,

with a seven cent premium for plain colors. Total production of styrene resins in 1944 was about 10,500,000 pounds.

Extruded Shapes. Formerly restricted to molded shapes, polystyrene is now available in a wide variety of extruded forms also. These in-

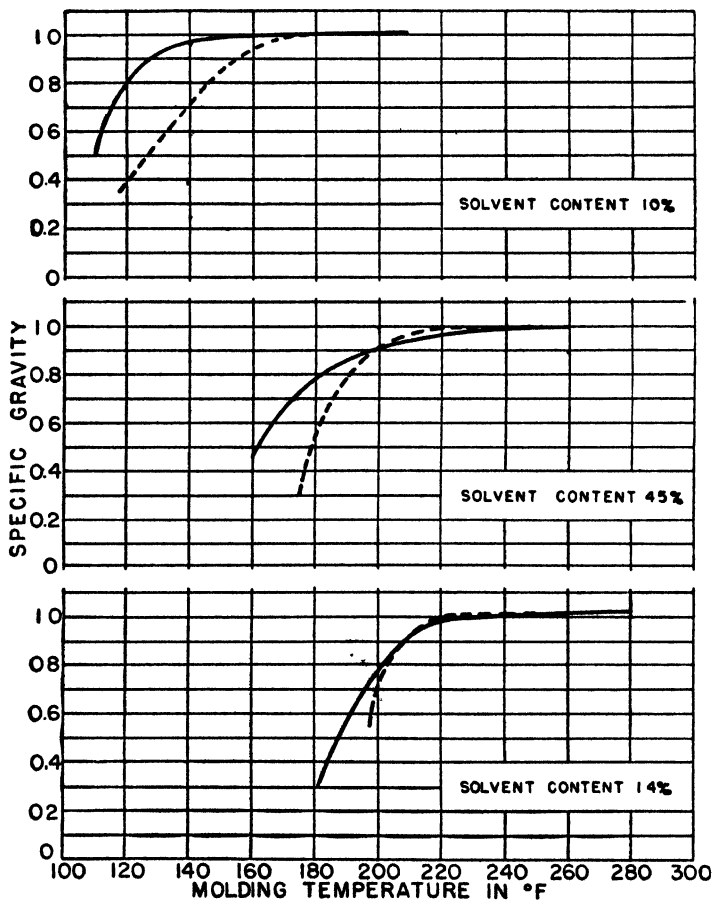


Figure 187. Density of molded "Polyfibre" according to solvent content and molding conditions.—Press-molded for three minutes at 15 lb/sq in --- Bag-molded for fifteen minutes at 15 lb/sq in. (Goggin and Bradshaw¹³)

clude solid rods and tubes up to several inches in diameter, square rods, and sheets.

Extruded polystyrene monofilament, down to very fine denier, is under development. "Polyfibre," described later, is one such material. When cold-stretched, polystyrene fiber possesses greater strength and decreased brittleness, although it is subject to retraction upon warming. Cold-

stretching of polystyrene monofilaments is practiced upon strands up to about $\frac{1}{8}$ inch diameter, the strength increase caused thereby decreasing as the diameter is increased.

"Polyfibre." Under this trade name, the Dow Chemical Company has developed large bats of oriented polystyrene fibers, laid parallel to each other at crosswise directions. Bat dimensions at present are 14 inches by 10 feet. Fiber diameters average two microns, running up to five. By way of comparison, cotton fibers average 15 and wool, 29 microns. Apparent density of the batting is about 0.05. It is produced contain-

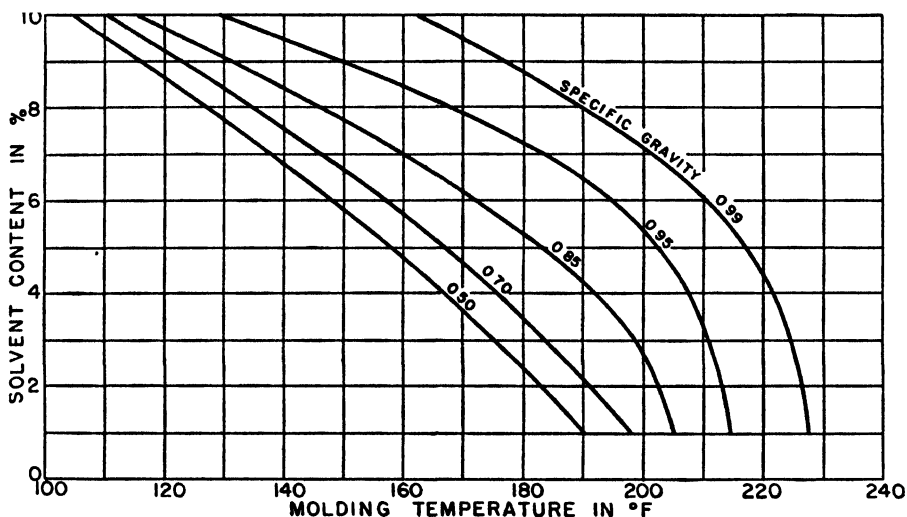


Figure 188. Molding conditions producing "Polyfibre" of constant density. Press-molded 3 minutes at 15 lbs./sq in. (Goggin and Bradshaw¹³)

ing a small amount of solvent, a factor which influences molding conditions and final properties.

"Polyfibre" may be used as a heat or sound insulator within temperature ranges where its thermoplasticity permits. It is of especial interest, however, as a molding material. Because of its large surface area, it can be compression molded in shorter cycles and at lower temperatures than can be used with conventional molding powders. Its greatest interest lies in the fact that it has opened up the field of low pressure molding of large areas to thermoplastics. Its large surface area not only facilitates rapid heating, but the stretched, oriented fibers retract upon heating so that they exert internal pressure which eliminates the necessity for application of external high pressure during molding. Combination of these two factors makes it possible to use inexpensive metal molds and rubber bag molding methods. Densities as low as 0.4, ranging upwards to

the full density of polystyrene, 1.05, can be obtained by suitable adjustment of molding conditions as shown in Figures 187 and 188. Controlled density gradients throughout molded "Polyfibre" can also be obtained.

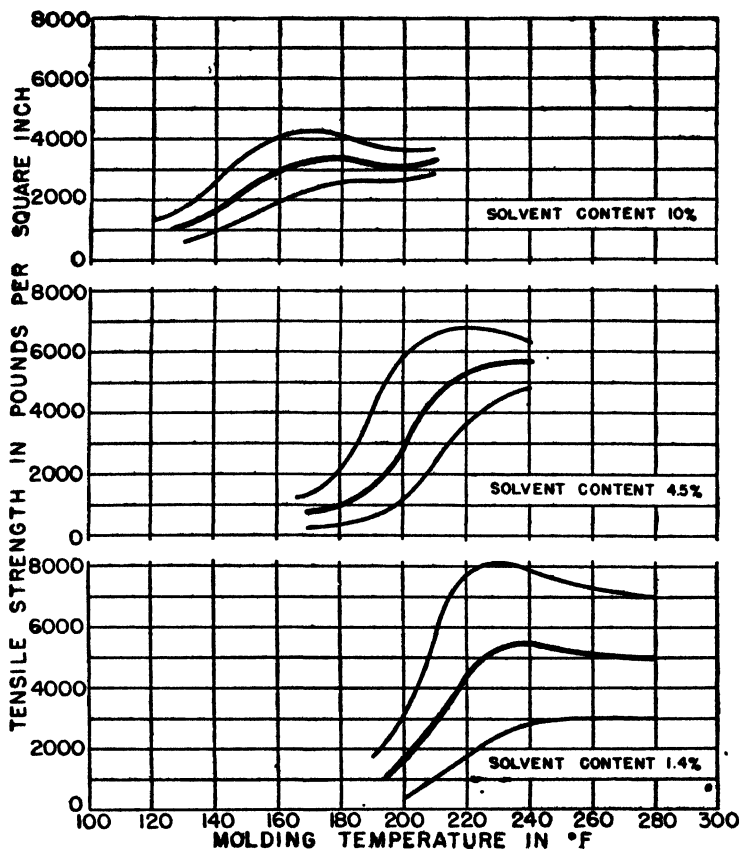


Figure 189. Tensile strength of bag-molded "Polyfibre." (In each group of curves the top one is with grain, the center is average strength, random fibers, the bottom is across grain.) (Goggin and Bradshaw¹⁵)

Strength characteristics can be adjusted to some extent by controlling the arrangement of successive plies of "Polyfibre" batting, as shown in Figure 189 where *random fibers* means that the bats are laid up alternately at 90° to each other.

Although tensile strength of molded "Polyfibre" is less than that of injection molded plastic, heat resistance is substantially the same and water resistance is not greatly affected, as can be seen from Figure 190.

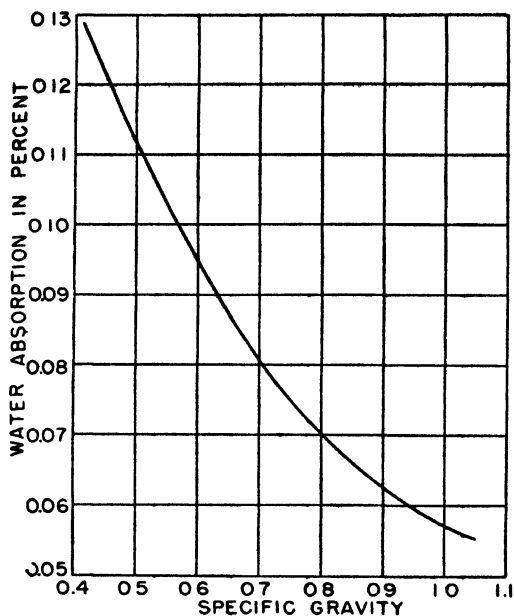


Figure 190. Water absorption of molded "Polyfibre" vs. specific gravity. (Goggin and Bradshaw¹⁸)

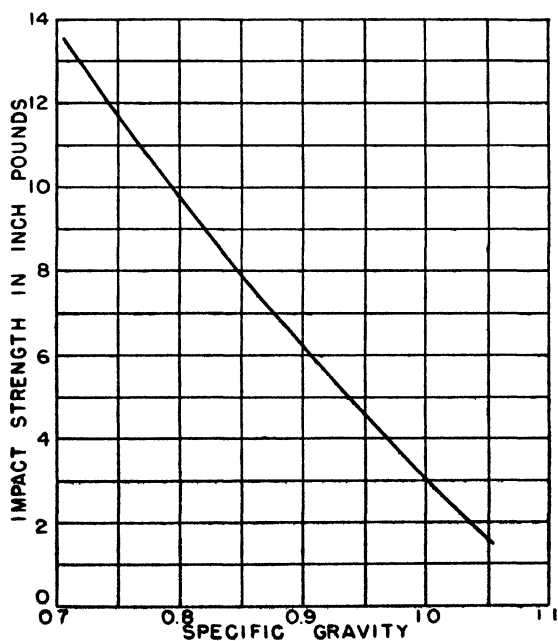


Figure 191. Relation of impact strength of molded "Polyfibre" to density. (4 per cent solvent content. $\frac{1}{2} \times \frac{1}{8}$ in. unnotched bars.) (Goggin and Bradshaw¹⁸)

Some degree of orientation appears to remain in the molded article, even at maximum density, so that impact strengths are much improved over that of standard molded polystyrene. The relation of impact strength, as measured on $\frac{1}{2} \times \frac{1}{8}$ inch unnotched specimens, to density of molded "Polyfibre" is shown in Figure 191.

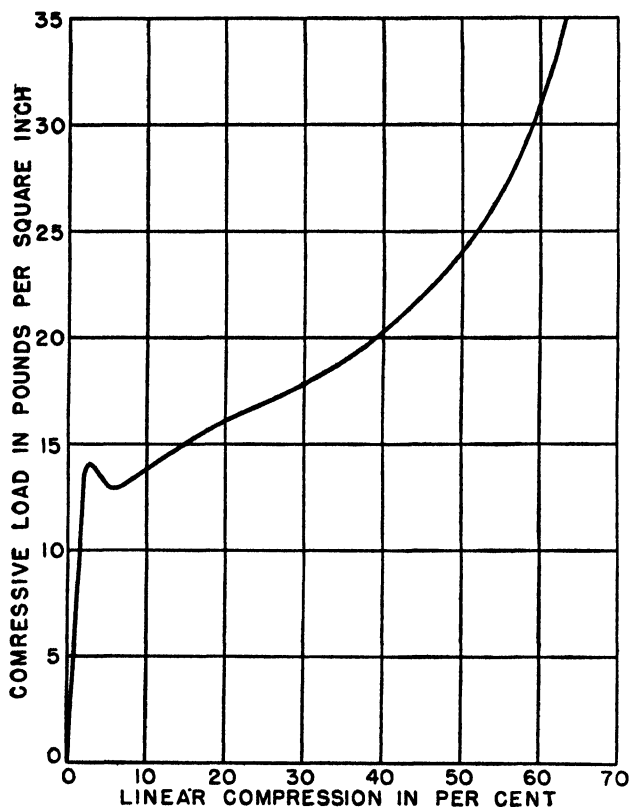


Figure 192. Compressive strength curve for expanded polystyrene ("Styrofoam") of density 1.5 lb/cu ft. (Mc-Cuaig and McIntire²²)

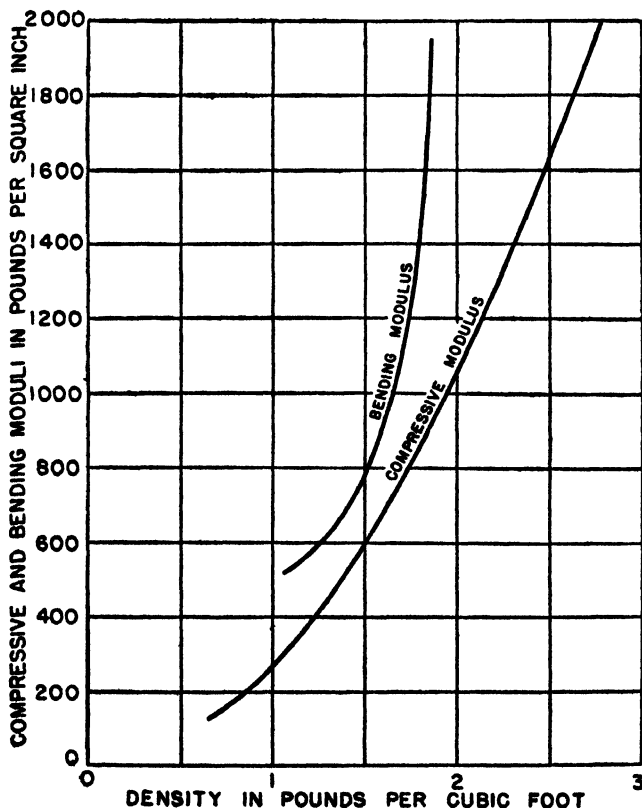
Electrical properties of molded "Polyfibre" are excellent. Its dielectric constant is even less than that of conventional high-pressure molded polystyrene and decreases as density decreases.

Table 68 compares the properties of molded "Polyfibre" with those of conventional molded polystyrene.

Expanded Polystyrene. The Dow Chemical Company has recently placed on the market an expanded form of polystyrene under the trade name "Styrofoam." This product consists of a coherent, relatively strong

Table 68. Comparison of Properties of "Polyfibre" at Various Densities with Polystyrene¹³

	Polystyrene Standard Molding Grade	"Polyfibre" (4.5% Solvent Content) Random Fiber Layup Density				
		0.60	0.70	0.80	0.90	1.01
Specific volume, cu in/lb	26	46	39	34	30	28
Tensile strength, lbs/sq in (ave.)	7,000	2,000	2,300	2,600	3,200	3,900
Impact strength, in-lbs ($\frac{1}{2} \times$ $\frac{1}{8}$ in, unnotched)	1-2	—	13.5	9.5	6.0	3.0
Flexural strength (maximum)	14,000	2,200	3,600	6,000	9,800	15,000
Hardness (Rockwell superficial)	90-93	—	—	15	49	80
Dielectric constant, 1,000,000 cycles	2.55	1.72	1.85	1.99	2.20	2.40
Heat distortion, °F	175	160	160	160	160	160
Water absorption, %	< 0.05	0.1	< 0.1	< 0.1	< 0.1	< 0.1

Figure 193. Compressive and bending moduli of expanded polystyrene ("Styrofoam") as a function of density. (McCuaig and McIntire²²)

cellular mass of discontinuous air pockets—from $\frac{1}{8}$ to $\frac{1}{4}$ inch average diameter—each totally enclosed in a continuous polystyrene membrane. It is about forty-two times more voluminous than molded polystyrene and is at present available in a grade having an apparent density of 1.5–2 lbs/cu ft. Other densities have been produced on a small scale. Typical

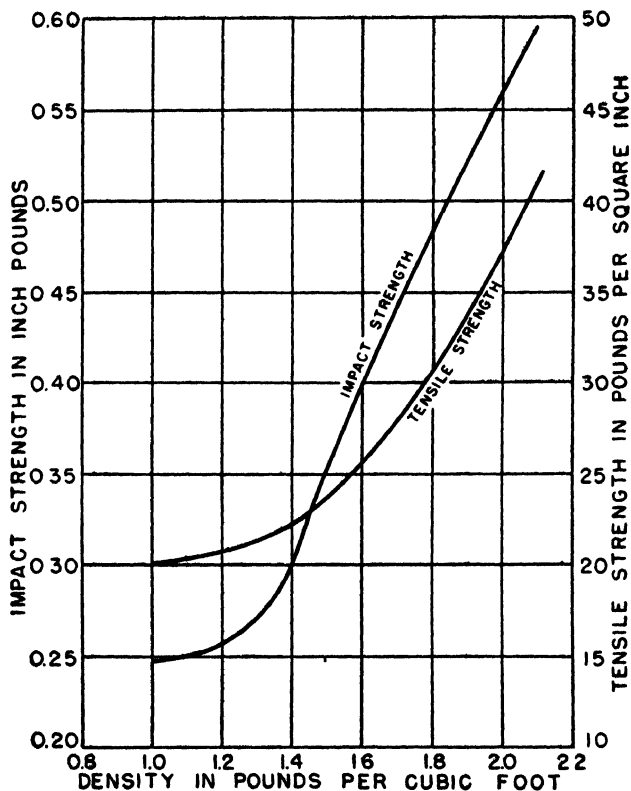


Figure 194. Impact strength and tensile strength of expanded polystyrene ("Styrofoam") as a function of density. (Impact strength specimens: $\frac{3}{8} \times \frac{1}{2}$ inch.) (McCuaig and McIntire²²)

properties are shown in Figures 192 to 195. Principal applications are based upon its buoyancy, low density, heat insulating characteristics, electrical properties, and moisture resistance. It is highly resistant to mold growth, rot, and decay. Its upper operating temperature is 170° F.

Foil. Polystyrene is available under the trade name "Polyflex" as foil in thicknesses of 0.001 and 0.020 inch. Ribbons and sheets are produced in both clear and light purple grades, the latter in order to mask discoloration (yellowing) during service. Polystyrene foil is used especially

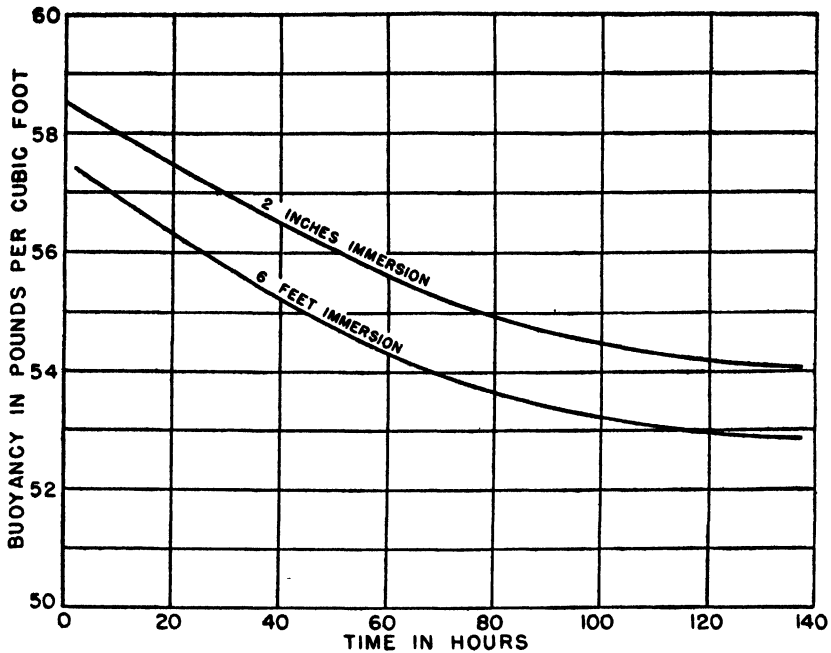
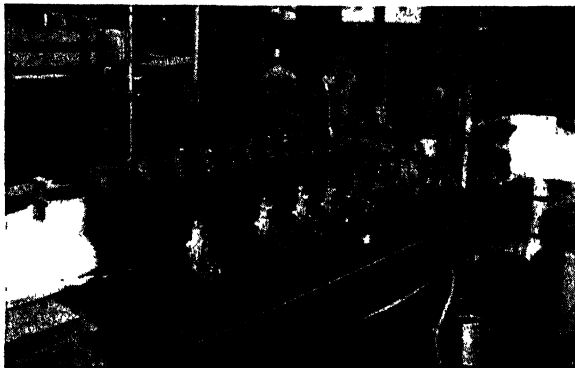


Figure 195. Buoyancy of expanded polystyrene ("Styrofoam") after long-continued immersion in water. These curves illustrate the exceptional strength of cell structure of this material. (*McCuaig and McIntire*²²)



Courtesy Plax Corp.

Figure 196. Machine for extruding polystyrene sheet material.

as insulation for wound coils and condensers. Brittleness is overcome by a two-way stretch which affords a means of orienting the molecules in both directions.

Filled Polystyrene

"Styramic." Although polystyrene is usually supplied in the form of molding powders and stock shapes consisting of pure polymer, with or without coloring material (more commonly without), it is possible not only to plasticize it, but also to load it with any of the commercial fillers. Such practices, however, have not been generally adopted because there seem to be no advantages to be gained while, on the contrary, many of the valuable characteristics of polystyrene are lost. One notable exception exists. It is a product of the Monsanto Chemical Company sold under the trade name "Styramic." It consists of polystyrene filled with a high-melting high chlorine content "Aroclor," or chlorinated biphenyl. While the tensile and flexural strengths of polystyrene are about halved by filling in this manner, water absorption and dielectric strength are not greatly affected, and resistance to heat and flammability are much improved. "Styramic" has therefore been developed primarily as a superior high-frequency insulating material of greater heat resistance than polystyrene. Its "Aroclor" content lends nonflammability. Its density is 1.358, considerably higher than that of unfilled polystyrene. It machines more readily than polystyrene and is available as molding powder and in extruded sheet, rod, tube, and bar forms. It emits an even more pronounced metallic ring than polystyrene when struck sharply or dropped upon a hard surface.

Physical properties of "Styramic" listed by Monsanto are given in Table 69.

Miscellaneous Forms

Casting. Although much less common than with the methacrylates, polystyrene can be cast by polymerizing the monomer under heat in the presence of benzoyl peroxide, or by standing for several months at room temperature. It can also be used as an impregnant and polymerized *in situ*.

Lacquers. While polystyrene has been advanced as a component of lacquers and varnishes, its use in this manner is not, at the present time, to be recommended, for weather resistance, adhesion, flexibility, and color stability are all poor where it is used as a base for surface coatings. The hydrophobic nature of polystyrene also precludes its use as an adhesive applied to hydrophilic surfaces, such as wood or glass. Its use as an interlayer for safety glass is therefore impractical.

Table 69. Physical Properties of "Styramic" *

Formulations and Colors	Styramic 28 Gray Styramic 20 Natural
Granulations, ins	$\frac{1}{4}$
Screen Analysis Limits, % Through 3 mesh	100
Through 14 mesh	3
Recommended Molding Method	Inj., ext. & comp.
Compression Ratio	2.5-2.8
Injection Molding Temperature, ° F	325-450
Compression Molding Temperature, ° F	300-350
Injection Molding Pressure, lbs/sq in	10,000 and up
Compression Molding Pressure, lbs/sq in	500 to 5,000
Specific Gravity, 25°/25°	1.358
Specific Volume, cu ins/lb	20.4
Mold and Age Shrinkage, ins/in	0.0025 after 6 mos.
Heat Distortion, ° F	184-187
Flow Temperature, ° F	280
Water Absorption, 24 hrs, %	0.046
Burning Rate	Chars slightly but will not burn
Tensile Strength, lbs/sq in	3,000-3,500
Flexural Strength, lbs/sq in	6,000-7,000
Compressive Strength, lbs/sq in	10,000-12,000
Young's Modulus, in Tension	3.34×10^5
Impact Strength, Izod, ft lbs/in of notch	0.3
Rockwell Hardness	M72
Dielectric Constant, 300 kc, dry	2.55
Dielectric Constant, 300 kc, 96 hrs water immersion	2.60
Power Factor, 300 kc, dry	0.0004
Power Factor, 300 kc, 96 hrs water immersion	0.0004
Loss Factor, 300 kc, dry	0.001
Loss Factor, 300 kc, 96 hrs water immersion	0.001

The above values except where otherwise noted are determined on samples conditioned and tested at 25° (77° F) and 50% R.H.

* Manufacturers' data. The Monsanto Chemical Co.

Styrene Copolymers

The development of large scale production of cheap styrene in the rubber program has led to considerable diversification in the use of this unsaturate. This trend is likely to continue so that the future will undoubtedly see a number of new plastics based upon styrene, in addition to polystyrene itself. Both copolymers and heteropolymers of styrene are included in this growing family.

The use of styrene in conjunction with butadiene to form GR-S synthetic rubber is discussed in Chapter 20. Another elastomer of quite different properties, based largely upon styrene, is produced by the Dow Chemical Company under the trade name, "Styraloy." It, too, is treated in Chapter 20. "Pliolite" S-3, produced by the Goodyear Tire and Rubber Company, is an 85:15 styrene-butadiene copolymer. It is compatible with natural rubber and with several synthetic elastomers. Although it

is brittle at room temperature, it does not greatly raise the brittle point of elastomers with which it is compounded for the purpose of improving smoothness on extrusion or calendering and for reducing shrinkage. Important applications for "Pliolite" S-3 have been found in the field of electrical insulation.

Low-pressure, no-pressure laminating resins in which styrene is copolymerized with other unsaturates, especially unsaturated linear alkyds, have been developed under such trade names as "Laminai." These resins are described in Chapter 19.

Copolymers with Divinyl Benzene. Staudinger's theoretical studies of the behavior of divinylbenzene where copolymerized with styrene have been mentioned earlier in this chapter. Monomeric divinylbenzene, admixed with various diethylbenzenes and ethylvinylbenzenes, is available commercially in approximately 25 per cent solution. It can be copolymerized not only with styrene, but also with mixtures of styrene and dehydrated castor oil to yield relatively heat-resistant and solvent-resistant copolymers. Such compositions have been used to some extent as sealants for porous metal castings.

Dow's "Q-200" series of experimental plastics and General Electric's "Textolite" 1421 are apparently copolymers of styrene and divinylbenzene, although the specific nature of these products, particularly the latter, has not been disclosed by the manufacturers. Prices of the former products range from \$4.50 to \$5.00 per pound, while the latter costs from two to three times as much, depending upon shape. These products are available in cast forms and withstand higher temperatures than polystyrene. Q-200.3 can be compression molded.

Properties of "Q-200" plastics are compared with those of "Styron" in Table 70, while Table 71 lists the characteristics of "Textolite" 1421.

Copolymers with Nitrogenous Unsaturates. Under the trade-mark "Cerex," the Monsanto Chemical Company has developed a new series of thermoplastic, heat-resistant molding compounds containing only carbon, hydrogen, and nitrogen. The chemical identity of "Cerex" has not been disclosed by the manufacturer. It appears to be a styrene copolymer, possibly with acrylonitrile. "Cerex" plastics are transparent and range in color from yellow to dark amber. They can therefore be formulated in a multitude of transparent, translucent, and opaque colors. In many properties they are similar to polystyrene, but possess markedly superior heat resistance. Electrical loss properties at high frequencies are somewhat inferior to those of polystyrene, but because of their exceptional heat resistance, they can be used for many extremely low-loss applications where polystyrene is ruled out by heat considerations. A.S.T.M. heat distortion temperatures of various grades of "Cerex"

Table 70. Properties of Q-200 Plastics *

	Styron	Q-200.3	Q-200.5
Heat Distortion, ° C †	82	95-99	103-108
Linear Thermal Expansion, per ° C	$6-8 \times 10^{-5}$	8.3×10^{-5}	9.0×10^{-5}
Dielectric Constant, 1000 cycles	2.55	2.51	2.4-2.5
ultra high freq	2.55	2.51	2.4-2.5
% Power Factor, 1000 cycles	0.01	0.01-.013	0.012-.015
ultra high freq	0.05	0.05-.07	0.05-.09
% Water Absorption, 72 hours in boiling	0.04	0.02	0.02
Tensile strength, psi	7000	6000-8000	7000-9000
Elongation, %	2-5	2.7-3.0	2.9-3.3
Modulus of Elasticity, psi	$1.7-2.0 \times 10^6$	2.5×10^6	2.4×10^6
Hardness, Rockwell, Superficial	89	93	95
Impact, inch-pounds	1.0	1.4-2.1	1.3-1.9
Refractive Index	1.59	1.59	1.59
Specific Gravity	1.05	1.05	1.05
Resistant Resistance, Acids, Alkalies	Excellent	Excellent	Excellent
Aromatic Solvents	Dissolves	Swells	Swells
Machinability	Good	Excellent	Excellent
Moldability	Excellent	Compression molds with difficulty	Not recommended

Q-200.7, with a heat distortion around 120°, is somewhat more brittle than Q-200.5 and is more difficult to machine because of its greater hardness. It does, however, grind quite well. Its power factor may be as high as 0.12% at ultra high frequency.

* Manufacturers' data. The Dow Chemical Co.

† Temperature at which a 5 mil deformation is observed in a $\frac{1}{10} \times \frac{1}{2}$ in sample supported flatwise on 1 in centers and loaded in the center with a 260 gm-weight. This temperature corresponds closely to values obtained by the Standard A.S.T.M. test.

Table 71. Properties of G. E. "1421" Cast Resin *

Color	Pale yellow to water white
Machinability	Good, similar to brass
Specific gravity	1.04 to 1.06
Impact (Dynstat)	0.07 to 0.08 ft lbs
Flexural strength (Dynstat)	7500 to 10,000 lbs/sq inch
Dielectric constant (300 MC)	2.4 to 2.5
Power factor (300 MC)	0.0006 to 0.0009
Solvent resistance	Generally insoluble in most solvents, but swells in aromatic hydrocarbons
Thermal expansion	$8.25 \times 10^{-5}/^{\circ}\text{C}$
Heat distortion, A.S.T.M.	75-80°
Fusibility	Nil; the material will soften at increased temperatures but will not melt. Without load it will retain its form up to 200° being rubber-like only at these temperatures. On cooling it assumes its hard form again.
Water absorption	Less than 0.1% in 24 hrs.

* Manufacturers' data. The General Electric Co.

range from 195 to 300° F, that of "Cerex" X214, now on the market, being 220–230° F.

"Cerex" is resistant to acids and alkalies. It can be boiled in water and in battery acid without harm. It is insoluble in carbon tetrachloride and aliphatic hydrocarbons, but is dissolved by aromatic and most chlorinated hydrocarbons. It does not contain plasticizer.

"Cerex" may be fabricated by injection, compression, extrusion or film-forming methods. In molding by injection, the mold should be maintained at 180 to 220° F to avoid hardening in the sprue or runners. Cylinder temperatures of 370 to 450° F are recommended. Serious decomposition begins to occur about 470° F, resulting in formation of gas and a thin black syrup at 500° F. Discoloration commences upon prolonged exposure to temperatures of about 400° F.

Properties of "Cerex" X214 are listed in Tables 72 and 72a.

Principal applications to date have been in radar and other military electronic equipment. Numerous uses are proposed, including surgical and other sterilizable instruments, dishes, and containers, coil forms, battery jars, and various electrical appliances. Price is in the higher bracket of general utility thermoplastics.

Other Copolymers. The Rohm and Haas Company has recently announced "Plexene" M, a light amber-colored styrene copolymer modified with another unsaturate of as yet undisclosed identity. It possesses better heat resistance, strength, and machining qualities than are shown by polystyrene itself. Physical properties are listed in Table 73. "Plexene" M is currently available in limited quantities at about 85 cents per pound.

Heteropolymers with Maleic Anhydride. Although maleic anhydride does not polymerize alone, it can be copolymerized with styrene to yield a heteropolymer possessing the unit structure which appears on page 418. This product is available commercially in the form of a 20 per cent aqueous solution of its corresponding ammonium salt. It is sold by the Bakelite Corporation under the designation "ammonium salt of 'Vinylite' SYHM resin." Formerly restricted to a very few highly specialized applications, this water-soluble substance now gives promise of more general utility as a protective colloid, binder, and reinforcing agent in such fields as printing inks and paper.

Polymers of Substituted Styrenes

Alkyl Styrenes. Various polymers of *o*-, *m*-, and *p*-methyl styrenes have received some study. Straight polymers of these compounds do not appear to be commercialized at present, but a series of resins ranging from viscous liquids through tacky to brittle and finally tough, horny solids has been placed on the market under the trade name "Pic-

Table 72.¹⁵ Comparison of Properties of "Cerex" and Polystyrene *

	"Cerex"	Polystyrene
Injection molding temp.,		
Cylinder, ° F	370-500	400-450
Mold, ° F	170-250	150
Specific gravity	1.07	1.05-1.07
Flexural strength, psi	13,000	8,000-10,000
Deflection, in	0.169	0.110-0.130
Impact strengths,		
Charpy-notched, ft lb/in	0.46	0.30-0.37
Izod-notched, ft lb/in	0.40	0.30-0.40
Izod-unnotched, ft lb/in	3.48	2.64
Distortion temp. std., ° F	212-230	168-176
Rockwell hardness	M100	M80-M90
Dielectric strength, v/mil	510	500-700
Dielectric constant,		
60 cycles	—	2.5-2.6
1,000 cycles	2.72	2.5-2.6
1 megacycle	2.76	2.5-2.6
Power factor,		
60 cycles	—	0.0001-0.0003
1,000 cycles	0.0024	0.0001-0.0003
1 megacycle	0.0024	0.0001-0.0003
Arc resistance, sec	69	61
Burning rate	Slow	Slow
Water absorption, A.S.T.M. 24 hr, per cent	0.30	0.05
Effect of,		
Weak acids	None	None
Strong acids	Oxidizing acids attack	Oxidizing acids attack
Weak bases	None	None
Strong bases	—	—
Solubility	Soluble in aromatic and chlorinated hydrocarbons	Soluble in aromatic and chlorinated hydrocarbons
Clarity	Amber transparent	Transparent
Color possibilities	Extensive	Unlimited

* Values determined under appropriate A.S.T.M. test methods.

Table 72a. Results of 48-Hour Boiling of Compression-Molded Disks of "Cerex" and Other Plastics¹⁵

Material	Weight Change (%)	Thickness Change (%)	Diameter Change (%)	Appearance Change
Phenolic, general purpose	+ 9.6	+ 9.2	+ 1.95	Surface roughened
Urea, general purpose	- 2.0	- 12.9	+ 2.74	Disintegrated
"Cerex" X-214	+ 0.8	+ 1.5	none	No effect

Table 73. Properties of "Flexene" M*

Property	Test Method	Test Conditions	Data
Specific gravity	A.S.T.M. D71-27		1.08
Tensile strength	A.S.T.M. D638-42T	1/8" maximum	10,000 psi
		1/8" rupture	10,000 psi
Flexural strength	A.S.T.M. D650-41T	1/4" maximum	10,000 psi
		1/4" rupture	10,000 psi
		Maximum	16,000 psi
		Rupture	16,000 psi
Compressive strength	A.S.T.M. D695-42T	Modulus elasticity	500,000 psi
		Deflection	0.2 in
		Unnotched	15,000 psi
Impact strength	A.S.T.M. D256-41T	(1/2" X 1/2" section)	3.2 ft lbs
		Notched	1.0 ft lb
Heat distortion	A.S.T.M. D648-45T	(per inch molded notch)	
		1/2° C/min-264 psi	85° (185° F)
Flow temperature	A.S.T.M. D569-43	2° C/min-264 psi	90° (194° F)
		2° C/min-66 psi	102° (216° F)
		At 1500 psi	145 ± 5° (293 ± 9° F)
		2 hrs @ 80° (176° F)	0.2 mils per inch
Shrinkage of injection molded bar	Air oven heating	2 hrs @ 90° (194° F)	0.5 mils per inch
		2 hrs @ 100° (212° F)	6.0 mils per inch
Rockwell number	R & HP-20*	1/4" ball, 100 kg	M77
		CS 10/500g	
Abrasion resistance	LP406a-1092	25 revs	11 %
		(% parallel light trans)	

* See "Flexiglas — Mechanical Properties" (Rohm and Haas Co.) pages 12-14 for description of test method.

			As Received	Accelerated Aging — 24 Hrs.
Light transmission			Parallel	39 %
			Total white	44 %
			Haze	11 %
Accelerated weathering	LP-406a-6021 (200 hours)		Crazing	None
			Discoloration	None
			Warping	None
			Unmolding	None
			Short time test	350 \pm 25 volts/mil
Dielectric strength, 25° (77° F) Dielectric constant	A.S.T.M. D149-40T A.S.T.M. D150-42T	60 cycles 1000 cycles 1,000,000 cycles	Bridge method	3.0 \pm 0.3
			Bridge method	3.0 \pm 0.3
			Susceptance method	3.0 \pm 0.3
		60 cycles 1000 cycles 1,000,000 cycles	Bridge method	1.0 \pm 0.3 %
			Bridge method	0.8 \pm 0.3 %
Power factor, 25° (77° F)	A.S.T.M. D150-42T		Susceptance method	1.0 \pm 0.3 %
				140 \pm 10 seconds
				0.17-0.23
Arc resistance Loss factor	A.S.T.M. D495-42 A.S.T.M. D150-42T	60 cycles 1000 cycles 1,000,000 cycles	Bridge method	0.16-0.21
			Susceptance method	0.06-0.09
Burning rate Odor			Slow	
			None	

Resistance to chemical reagents	A.S.T.M. D543-41T	Percent weight change after 7 days @ 25° (77° F) immersion in:	
(A change in weight of 1% or less is considered negligible.)		Sulfuric acid 30%	0.19
		Sulfuric acid 3%	0.36
		Nitric acid 10%	0.34
		Hydrochloric acid 10%	0.27
		Acetic acid 5%	0.35
		Oleic acid	0.02
		Sodium hydroxide 10%	0.30
		Sodium hydroxide 1%	0.36
		Ammonium hydroxide 10%	0.41
		Sodium carbonate 2%	0.33
		Sodium chloride 10%	0.32
		Hydrogen peroxide 3%	0.37
		Distilled water	0.37
		Ethyl alcohol 50%	0.38
		Ethyl alcohol 95%	0.65
		Acetone	Dissolved
		Ethyl acetate	Dissolved
		Ethylene dichloride	Dissolved
		Carbon tetrachloride	0.30
		Toluene	Dissolved
		Gasoline (heptane)	0.20

* Manufacturers' data. Rohm and Haas Company.

colastic," by the Pennsylvania Industrial Chemical Corporation. These products are said to be produced from styrene type materials which contain homologs thereof. Ball and ring melting points range from 5 to 150°. These products are not applicable to molding operations.

Chlorostyrenes. Although refractory plastics can be obtained by chlorination of polystyrene, more interesting products result by polymerization of monomeric styrenes in which from two to five of the nuclear hy-

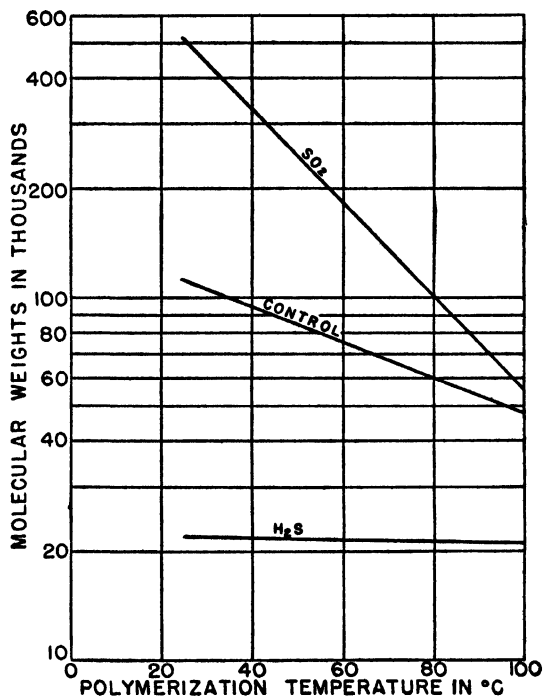


Figure 197. Effect of sulfur dioxide and hydrogen sulfide on the molecular weight of dichlorostyrene polymers. (Adapted from Michalek and Clark²⁴)

drogen atoms are replaced by chlorine. In this family, dichlorostyrene is at present best known. Six isomers of this compound exist. All of them except the 3,4-derivative yield polymers which are soluble in aromatic hydrocarbons, chlorinated hydrocarbons, and certain esters and higher ketones. They are insoluble in aliphatic hydrocarbons, the lower alcohols, ethers, and glycols. The polymer derived from 3,4-dichlorostyrene, on the other hand, is insoluble in toluene and carbon tetrachloride, but is soluble in methyl ethyl ketone. Sulfur dioxide facilitates chain growth, as shown in Figure 197.

Polydichlorostyrene is water white, resembling polystyrene itself in appearance, but of higher density. Its A.S.T.M. heat distortion point is 236° F or higher, depending upon the specific product. Because of the nuclear character of the chlorine atoms, there is none of the tendency toward decomposition encountered in aliphatic chlorine compounds and stabilizers are unnecessary. Tensile and impact are slightly inferior to polystyrene. Its deformation under load is compared with that of polystyrene in Figure 198.

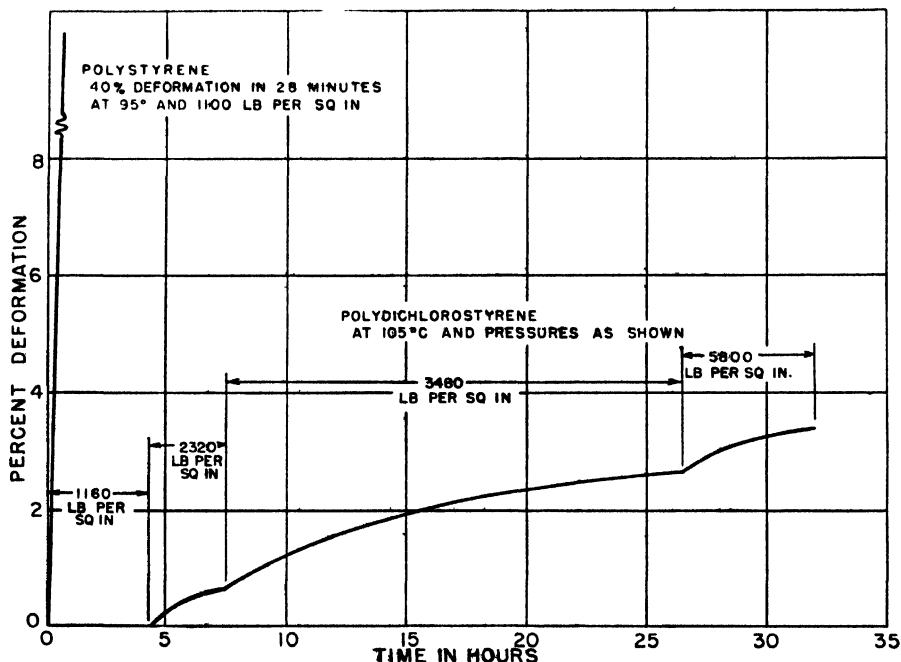


Figure 198. Deformation characteristics of polystyrene and polydichlorostyrene under load. (Jones and Brown¹⁶)

Properties of polydichlorostyrenes, sold under the trade names "Styramic HT" and "Mathieson" Plastic, are given in Table 74.

This plastic is at present premium priced, costing slightly less than \$15.00 per pound. Principal applications thus far have been in the field of military electronics.

For comparative purposes, properties of Monsanto's "Lustron" (polystyrene), "Ceretex," "Styramic," and "Styramic HT" are given in Table 75.

Dichlorostyrenes have been copolymerized with numerous other unsaturates, including butadiene. From this work has come a new elastomer, "Mathieson" rubber, which contains 30 to 40 per cent of dichlorostyrene.

Table 74. Properties of Polydichlorostyrene

Property	"Mathieson" * Plastic	"Styramic HT" ¹⁶
Molding qualities	good	very good *
Compression molding temp., ° F	350 to 425	360 to 400
Compression molding pressure, lb/sq in	2,000 to 5,000	—
Injection molding temp., ° F	475 to 525	475 to 550
Injection molding pressure, lb/sq in	10,000–30,000	—
Specific gravity	1.39 to 1.40	1.38
Refractive index, n_D	1.62 to 1.64	—
Flammability, in/min (A.S.T.M.—D635–41T)	self-extinguishing	self-extinguishing
Tensile strength, lb/sq in	4,600 to 7,460	¹
Modulus of elasticity, lb/sq in $\times 10^5$	5.0 to 7.0	—
Flexural strength, lb/sq in	14,000–19,000	¹
Impact strength, ft lbs/in of notch (A.S.T.M.—D256–41T)	1.0 to 1.5	¹
Hardness, Rockwell	M100	M103
Distortion under heat, ° F	240 to 265	236
Dielectric strength, volts/mil	370	—
Dielectric constant	2.55 to 2.65	—
1,000 cycles	—	2.62
1,000,000 cycles	—	2.62
Power factor (per cent)	< 0.1	—
1,000 cycles	—	0.0002
1,000,000 cycles	—	0.0002
Water absorption, 24 hours (per cent)	0.02	0.03
Effect of weak acids	none	¹
Effect of strong acids	none	¹
Effect of weak alkalies	none	¹
Effect of strong alkalies	none	¹
Effect of organic solvents	soluble in aromatic and chlorinated solvents	¹
Machining qualities	—	very good
Effect on metal inserts	inert	—
Clarity	transparent	¹
Color possibilities	unlimited	¹

* Moldability in extrusion machines is excellent.

¹ See Table 75.

This material is reported to possess much better oil resistance, tensile strength, elongation, tear resistance, flex cracking resistance, and resistance to deterioration upon heat aging than GR-S.

Vinyl-*t*-butylphenol. Vinyl-*t*-butylphenol, manufactured by reaction of acetylene with *t*-butylphenol, is polymerized to "Koresin," a General Aniline & Film Corporation product capable of imparting tack to GR-S. This material is discussed further in Chapter 20.

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Table 75. Comparison of Properties of Monsanto's Styrene Plastics²⁵

	"Lustron"	"Ceres X-214"	"Styramic"	"Styramic HT"
Specific gravity	1.05-1.07	1.08	1.358	1.38
Clarity	transparent (water white) unlimited	transparent (light amber) extensive	opaque	transparent (water white) unlimited
Color range			gray and natural only	
Odor	none	none	none	none
Taste	none	none	none	none
Rockwell hardness	M80-M90	M100	M72	M103
Burning rate	slow	slow	chars slightly but will not burn	self-extinguishing
Molding methods	injection compression extrusion excellent very good 6,000-7,000	injection compression excellent very good 13,750 0.35-0.45 220° F-230° F 0.30% same as Lustron	injection compression extrusion excellent very good 3,000-3,500 6,000-7,000 0.3 184° F-187° F 0.046% same as Lustron	injection compression extrusion excellent very good 5,400 8,750 0.27 236° F 0.03% same as Lustron
Molding qualities				
Machining qualities				
Tensile strength, psi	8,000-10,000			
Flexural strength, psi	0.3-0.4			
Impact strength, Izod, ft lbs per in notch	168° F-176° F			
Heat distortion point, A.S.T.M.	0.05%			
Water absorption after 24 hours' immersion	none except strong, oxidizing acids attack			
Effect of acids	none			
Effect of alkalis	soluble in aromatic and chlorinated hydrocarbons			
Solubility	boiling water distorts and crazes	boiling water has no effect	boiling water distorts and crazes	boiling water has no effect
Effect of hot water				
Electrical properties	excellent	good	excellent	excellent
at low frequencies	excellent	good	excellent	excellent
at high frequencies	excellent	fair	very good	excellent
at ultra-high frequencies				

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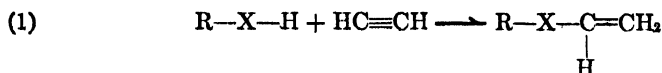
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Chapter 17

Polyvinyl Carbazole

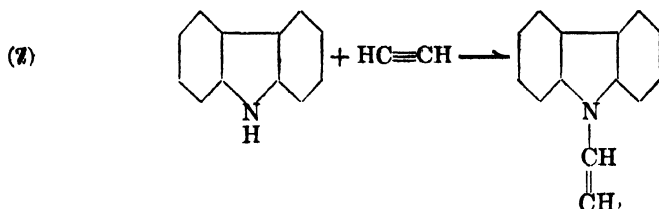
Monomer

Under carefully selected conditions, a variety of vinyl compounds can be prepared from acetylene by addition of alcohols, amines, mercaptans, carboxylic acids, and other compounds across the triple bond. The production of vinyl ethers according to this reaction has been discussed in Chapter 16. The general equation is:



where R is an organic radical and X is O, NR' , S, or CO_2 .

This reaction has been applied with particular success to carbazole, the product being the corresponding N-vinyl derivative:



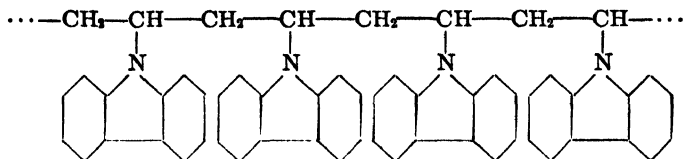
In this synthesis, alkali metal hydroxides or alcoholates, potassium carbazole, and other strongly alkaline substances are effective catalysts. Reaction can be still further facilitated and yields can be increased by use of certain auxiliary catalysts in conjunction with the alkaline materials just mentioned. Among such secondary catalysts, metallic zinc and certain zinc compounds, ammonia, and heterocyclic nitrogen bases like pyridine, quinoline, isoquinoline, and their derivatives are especially meritorious. According to patent disclosures, reaction is carried out in the absence of air under pressures in the order of 20 to 25 atmospheres and at temperatures in the neighborhood of 180° . The acetylene is diluted with an inert gas such as nitrogen. Ammonia may serve the dual purpose of diluent and secondary catalyst. The carbazole is preferably reacted in the form of a paste prepared by mixing it with a lower ali-

phatic alcohol or glycol, or with a hydrocarbon such as tetralin, decalin, benzene, or toluene.

Vinylcarbazole is a crystalline compound which melts at 66–67° and boils at 170–180° under 15 mm.

Polymer

Like styrene, vinylcarbazole can be polymerized to a linear thermoplastic, a portion of whose structure may be written as follows:



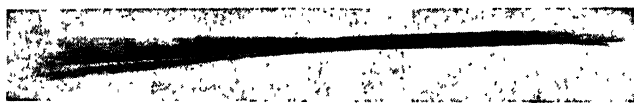
Polyvinylcarbazole is gray colored to light brown. In thin layers it is translucent. It resembles polystyrene in electrical properties, but possesses much superior heat resistance and can therefore be operated at higher temperatures and under relatively high voltage. It is outstanding in low power factor, high dielectric strength, high corona starting voltage, and high volume and surface resistivities. Its dielectric constant is uniform up to ultra high frequencies, varying with temperature only in accordance with its thermal expansivity. Its water absorption is exceptionally low, being comparable with that of polystyrene. It possesses poorer mechanical properties, however, than the latter plastic. In particular, it is more brittle and exhibits lower flexural strength.

Polyvinyl carbazole is resistant to dilute acids, alkalis, and hydrogen fluoride. It is attacked by concentrated nitric and sulfuric acids. It is insoluble in aliphatic and saturated cyclic hydrocarbons, as well as turpentine, alcohols, ethers, fatty oils, and carbon tetrachloride. It is readily dissolved by aromatic hydrocarbons and certain chlorinated solvents such as chlorobenzene and *o*-dichlorobenzene. It dissolves somewhat less readily in methylene dichloride, ethylene dichloride, and trichloroethylene. Ketones and some esters swell it.

Polyvinylcarbazole is slightly discolored by exposure to light, but it is unaffected by oxygen except at elevated temperatures.

Unplasticized polyvinylcarbazole possesses the remarkable characteristic of developing a pronounced macro-fibrous structure upon extrusion or injection molding. Where the softened material is forced through an orifice, it emerges not as a rod of diameter equal to that of the die, but rather as a bundle of individual fine, rigid fibers possessing improved strength properties because of molecular orientation. Although this behavior requires consideration in injection molding and extrusion of the

plastic, it affords a unique method of improving the mechanical characteristics of compression molded articles without addition of large amounts of plasticizer and without incorporation of extraneous fibrous materials of poorer electrical properties. Polyvinylcarbazole fibers, produced by extrusion, can be chopped into short lengths and used as a fibrous filler for compression molding powders based upon the powdered resin in which only sufficient plasticizer is incorporated to make it moldable at temperatures slightly below the softening point of the fibers. This unusual method of formulating compression molding powders dictates exceptional attention to molding conditions so that neither relaxation of



Courtesy General Aniline & Film Corp.

Figure 199. Characteristic macro-fibrous structure of extruded polyvinylcarbazole.

fibers with consequent loss of strength, nor porous moldings with attendant high water absorption will result.

Despite its relatively poor mechanical properties, well-molded polyvinylcarbazole can be machined.

Thin films of this resin can be deposited from solutions in chlorobenzene or other solvents.

Domestic Products. Polyvinylcarbazole is now manufactured in limited amounts in the United States by the General Aniline & Film Corporation under the trade-mark "Polectron." It is a specialty plastic, relatively costly to produce. Various formulations are available for different applications. It can be molded by compression and injection methods. A special polymer can be formed as thin, flexible, transparent sheets and film for electrical purposes. Either alone or in combination with other materials it can be used for coating and impregnating applications.

"Polectron" is especially well adapted for service in the field of electronics where exacting mechanical requirements are not encountered, but where high operating temperatures must be met.

Properties of "Polectron" RK-102 are given in Table 76.

Foreign Products. Polyvinylcarbazole has been manufactured in Germany by the I. G. for several years under the trade name "Luvican." Three grades have been produced varying in heat resistance; some of them are believed to be copolymers with styrene. The most heat-resistant type has been marketed under the designation "M-150," so indicated be-

Table 76. Properties of "Polectron" Polymer RK-102 *

Dielectric Constant—25°	
1 kc to 100 mc	3.0
Power Factor—25°	
1 kc to 100 mc	0.0004-0.001
after 48 hrs water immersion—1 mc	0.0025-0.004
Dielectric Strength v/mil	
for 0.1 in thickness	750-1000 †
for 0.001 in thickness	3000
Volume Resistivity—ohm cm	10 ¹⁴ -10 ¹⁵
Surface Resistivity—25°	
50% Rel. humidity	10 ¹⁴ -10 ¹⁵
Linear Coefficient of Expansion per °C × 10 ⁶	45-75 †
Heat Distortion Temperature A.S.T.M.	100-150° †
Specific Heat	
cal/g/°C	0.3
Flexural Strength (-20° to 80°)	
lbs/in ²	4500-5500 ‡
Impact Strength	
ft lbs/in of notch	0.5-1.0 †
Specific Gravity	1.2
Molding Temperature	
Compression	180-240° †
Injection	230-330° †

* Manufacturers' Data. General Aniline & Film Corporation.

† Depending on plasticizer content.

‡ Special compression molded composition.

cause its heat stability, as measured by the German Martens test, is at least 150°. Corresponding Martens temperatures for polystyrene range from 64 to 74°.

Certain physical properties of "Luvican M-150" are listed in Table 77. Inasmuch as values are reported in terms of standard German tests, corresponding characteristics of polystyrene are given for purposes of comparison.

Injection molded articles can be made from "Luvican" M-150 by heating the cylinder of the machine to 250-280° and holding the mold at 80-130°.

Principal applications of "Luvican" have been in the fields of electrical insulation and electronics. Its chemical inertness has adapted it to use in filter plates. It has also been used as an adhesive for bonding mica in the production of pasted mica sheets.

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Table 77. Comparison of Certain Physical Properties of Polyvinylcarbazole and Polystyrene *

	Polyvinylcarbazole (Luvican M-150)	Polystyrene (Trolitul III)
Density	1.2	1.05
Flexural Strength (kg/sq cm) VDE 0302	600-800	800-1000
Impact Strength, Notched Bar VDE 0302 (cm kg/sq cm)	ca. 2	ca. 5
Hardness, VDE 0302 (kg/sq cm)	1400	1400
Heat Resistance, Martens (° C)	150	64
VDE 0302, Vicat (° C)	190	90
Fire Resistance (VDE 0305)	1	1
Specific Resistivity (ohm cms)	$> 3 \times 10^{12}$	$> 3 \times 10^{12}$
After 4 days at 80% relative humidity (ohm cms)	$> 3 \times 10^{13}$	$> 3 \times 10^{13}$
Dielectric Constant		
800 cycles	3.0	2.4
10 ⁶ cycles	3.0	2.4
Power Factor (%)		
800 cycles		
20° C	0.08	0.02
100° C	0.10	—
150° C	0.16	—
1,000,000 cycles	0.15	0.02
Dielectric Strength (50 cycles, 1 mm thickness)	—	50,000 volts
Arc Resistance	poor	very good

* Collected from *Kunststoffe*, **27**, 91 (1937) and **30**, 2 (1940). Test procedures are to be found in the "Vorschriften des Verbandes Deutscher Elektrotechniker E. V." (VDE). For an English translation of some of these tests as of 1924, see "Artificial Resins," by Johannes Scheiber and Kurt Sändig, translated by Ernest Fyleman, Appendix, pp. 411-442, London, Sir Isaac Pitman & Sons, Ltd., 1931.

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Chapter 18

Acrylic Resins

HISTORY

It was the 15th of September, 1940. For three months following the cataclysmic collapse of France, the tempo of the Battle for Britain had been increasing in fury until, on that day, it reached a climax of 400 Nazi planes attacking London. As a breathless world looked on, the dauntless R.A.F. downed 42 per cent of the invaders and sent the remainder fleeing back to their airdromes across the channel, a shattered and disorganized armada. In an official account of the fighting of that day, a British pilot described the end of a dog-fight with a Messerschmitt 109 in these words: "I saw his perspex burst and the enemy aircraft spun down."

Popular British adoption of the word "Perspex," trade-mark of an English methacrylate, as equivalent of airplane windscreen bears eloquent testimony to the spectacular manner in which acrylic resins grew from commercial infancy to military manhood in less than a decade.

Although industrial acrylics are of recent origin, their academic precursors are of respectable age. Acrylic acid itself was first prepared a century ago. The earliest observation of its tendency to polymerize appears to have been made by Linnemann in 1872. In the following year, Caspary and Tollens prepared not only the acid, but also its methyl, ethyl, and allyl esters. They reported that neither the methyl nor ethyl ester polymerized on standing for several months in sunlight. They did, however, obtain a polymer of allyl acrylate which they described as a clear, hard, transparent mass. They also made the penetrating remark that in this respect allyl acrylate resembles styrene, certain vinyl derivatives, acrolein, acrylic acid, and vinylidene chloride, all of which had previously been reported to polymerize upon being heated.

The earliest preparation of polymethyl acrylate was carried out by the Swiss chemist, G. W. A. Kahlbaum. In 1880 he devoted an entire paper to a physical-chemical study of this product. It is recorded that he

once astonished his fellow-worker, Säuffer, with a flexible "unbreakable" beer glass made of an acrylic polymer. From then until the acrylates appeared as commercial plastics in the late 1920's, numerous references were made in chemical literature to polymers of acrylic acid, methacrylic acid, and various derivatives thereof. In 1901, the German chemist, Röhm, completed a doctoral study of certain acrylic acid derivatives. Eleven years afterwards, he obtained the first patent in this field, and finally, in 1927, the firm of Röhm and Haas began limited production of polymethyl acrylate in Germany. Four years later still, the American associate of this firm initiated manufacture of the resin in the United States. It was produced under the trade name "Acryloid" for surface-coating applications and under the trade name "Plexigum," as an inter-layer in "Plexite" safety glass—the latter being fabricated by the American Window Glass Company.

In England, research by Hill and others for Imperial Chemical Industries, Ltd., led to development of a methyl methacrylate resin, and rights under their United States patents were granted to E. I. du Pont de Nemours and Company.

Late in 1936 the Röhm and Haas Company introduced rigid sheeting of methyl methacrylate resin under the name "Plexiglas," and E. I. du Pont de Nemours and Company announced the beginning of production of sheets, rods, tubes, and molding powder under the name "Pontalite." This name was subsequently changed to "Lucite." About a year later Röhm and Haas began the sale of molding powder under the name "Crystalite," which was later changed to "Plexiglas."

Because of their optical properties, the methacrylates have received popular ovation reserved for only a few commercial products. Their military applications, especially in transparent airplane enclosures, are now of vital importance. As a result of this fact, their production increased many fold during the recent war. Lack of scratch-resistance is one of their most serious drawbacks. Improvement in this respect was studied with some success a few years ago by the Norton Company and resulted in the temporary innovation of a relatively heat-resistant grade of methyl methacrylate sheeting with improved surface hardness. Manufacture of the latter has since been discontinued because its advantages have not been great enough to justify manufacturing difficulties. Other grades of heat-resistant methacrylates are currently available.

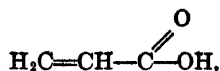
Lately the U. S. Eastern Regional Research Laboratory has made valuable contributions to our knowledge of acrylic polymers and copolymers.

Total production of acrylic resins for 1944 has been estimated at over 24,000,000 pounds, with total production of acrylic sheeting for the same year at more than 22,000,000 pounds.

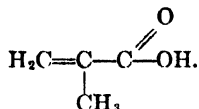
CHEMISTRY

Types of Acrylic Resins

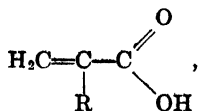
Acrylic acid,



and its functional derivatives such as the acid chloride, anhydride, nitrile, amide, anilide, and various esters polymerize under suitable catalytic influence to yield substances of high molecular weight. Alpha-substituted homologues of acrylic acid and its derivatives also polymerize in the same manner. Commercial representatives of the acrylic resins all stem from acrylic acid or from methacrylic acid,



Polymeric esters of ethacrylic and propacrylic acids,

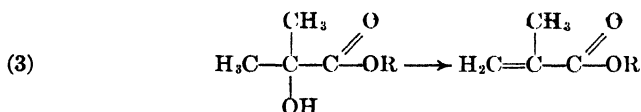
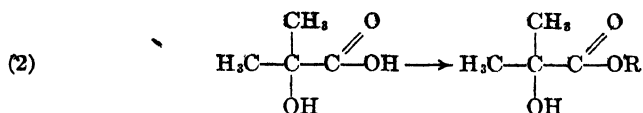
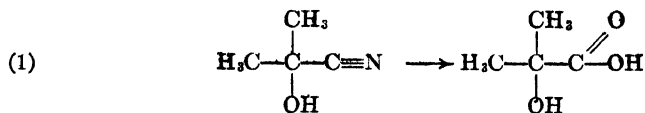


in which — R is — C₂H₅ or — C₃H₇, respectively, have been prepared, but are not manufactured commercially because of their cost, because of the sluggishness with which the monomers polymerize, and because of the soft and semi-liquid character of the polymers.

Although small amounts of polymethacrylic acid are manufactured for special purposes, the important plastics are all polymers or copolymers of esters of acrylic or methacrylic acid and the lower aliphatic alcohols. Oil-resistant elastomers are produced by copolymerization of acrylonitrile and butadiene, but these products are commonly classed as synthetic rubbers and will be discussed in Chapter 20.

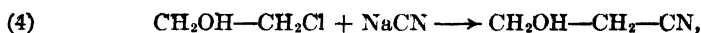
Monomeric Acrylates

Many different methods for preparing the monomeric esters of acrylic and methacrylic acids are reported in the scientific and patent literature. Only one general process, however, is used industrially today in this country. It involves hydrolysis, esterification, and dehydration of a corresponding saturated hydroxynitrile, as illustrated in equations 1 to 3 for the methacrylates.

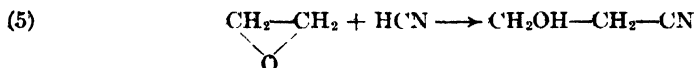


These three reactions can be carried out either consecutively or simultaneously, or the first two or last two may be combined.

The synthesis of the nitrile varies with its structure. In the case of hydraacrylonitrile, it is manufactured by reaction of ethylene chlorohydrin with sodium cyanide.

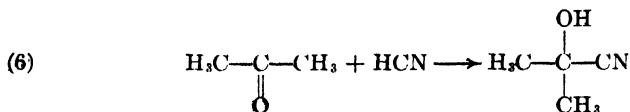


or by reaction of ethylene oxide with hydrogen cyanide:



Both methods are used industrially.

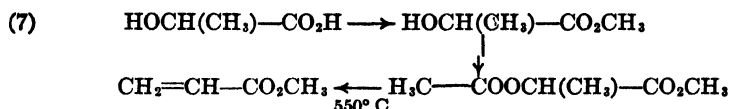
In the manufacture of esters of methacrylic acid, acetone is converted to acetone cyanohydrin by reaction with hydrogen cyanide:



Most of the acetone produced in the United States comes from propylene through isopropyl alcohol or from corn starch or molasses by fermentation. Hydrogen cyanide used in the manufacture of methacrylic esters may be obtained either by the action of acid on alkali or alkaline earth cyanides, or by catalytic dehydration of formamide which, in turn, is produced from an alkyl formate by reaction with ammonia.

The Sinclair Refining Company has recently developed commercial production of a variety of aliphatic nitriles, currently marketed by the Harshaw Chemical Company. These compounds appear to be manufactured catalytically from ammonia and various petroleum hydrocarbons. Acrylonitrile and methacrylonitrile are among the products now being offered to the trade.

Another method of manufacture of certain acrylic acid esters is currently under investigation in the Government's Eastern Regional Research Laboratory. It is directed toward the production of these compounds from lactic acid, obtained by fermentation of molasses, corn sugar, or milk sugar, availability and cost being the determining factor in the selection of raw material. Considerable promise is held for this process, which involves pyrolysis of the acetate of a lactic acid ester, such as methyl lactate:



The pyrolysis method is suitable for making methyl, tetrahydrofurfuryl, phenyl, tolyl, benzyl, and certain other acrylic esters, but is not applicable to the direct preparation of ethyl acrylate and similar higher alkyl acrylates.

A war-time development in Germany was the production of acrylic acid by reaction under pressure of acetylene, water, and carbon monoxide, using nickel carbonyl as catalyst. By using ethanol instead of water, ethyl acrylate was manufactured. Another recent German development in this field was large-scale production of acrylonitrile by direct addition of hydrogen cyanide to acetylene in aqueous hydrochloric acid solution, using a copper acetylide catalyst modified by addition of an alkali metal chloride.

Characteristic properties of the more important monomeric esters of acrylic and methacrylic acids are given in Table 78.

Table 78. Characteristic Properties of Esters of Acrylic and Methacrylic Acids

Ester	Boiling Point (°C)	Specific Gravity	Refractive Index
Methyl acrylate	80	0.954 (20/4)	1.4040 (n_D^{20})
Ethyl acrylate	99.5	0.923 (20/4)	1.4068 (n_D^{20})
<i>n</i> -Propyl acrylate	44 (40 mm)	0.9078 (20/4)	1.4130 (n_D^{20})
<i>n</i> -Butyl acrylate	35 (8 mm)	0.8998 (20/4)	1.4190 (n_D^{20})
Methyl methacrylate	100	0.950 (15.6°/15.6°)	1.417 ($n_D^{15.6}$)
Ethyl methacrylate	117	0.913 (15.6°/15.6°)	1.414 ($n_D^{15.6}$)
<i>n</i> -Propyl methacrylate	141	0.902 (15.6°/15.6°)	1.420 ($n_D^{15.6}$)
Isobutyl methacrylate	155	0.889 (15.6°/15.6°)	1.422 ($n_D^{15.6}$)
<i>n</i> -Butyl methacrylate	163	0.889 (15.6°/15.6°)	1.426 ($n_D^{15.6}$)

According to Rehberg and Fisher, the density (d_4^{20}) and refractive index (n_D^{20}) of the n -alkyl acrylates are given by the equations:

$$M/d = 1.185M - 9.5 \quad \text{and} \quad M/n = 0.6786M + 3.363,$$

respectively, where M is molecular weight (see also Figure 200).

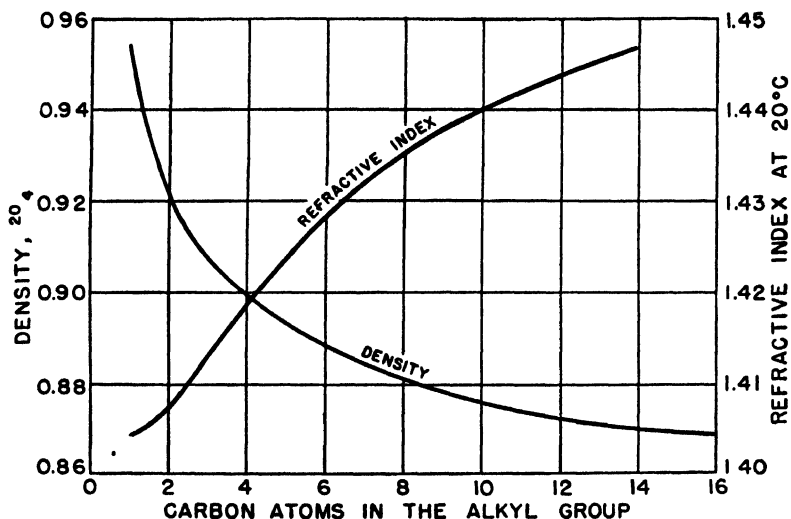
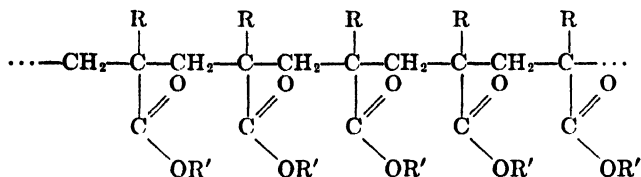


Figure 200. Refractive indices and densities of the monomeric n -alkyl acrylates. (Rehberg and Fisher²⁸)

Polymers

Factors Influencing Polymerization. The polymerization of esters of acrylic acid and methacrylic acid appears to be a chain reaction inasmuch as polymers of low molecular weight cannot be isolated during the reaction—only monomer and high polymers can be found present at any given instant, regardless of the extent of polymerization. The resulting polymers possess a linear structure, a segment of their chain corresponding to the general formula



where R is either H , in the case of the acrylates, or CH_3 , in the case of the methacrylates.

Polymerization of the acrylates is more rapid than that of the cor-

responding methacrylates under the same conditions. Both reactions are strongly exothermic and autocatalytic. For methyl methacrylate the heat of polymerization is about 80 calories per gram.

The polymerization of monomeric acrylates and methacrylates is accelerated by heat and light and such catalysts as oxygen, ozone, peroxides like those of the hydrogen, acetyl, lauroyl, succinyl, and benzoyl radicals, salts of perboric acid and persulfuric acid, and sulfur dioxide. Hydroquinone, pyrogallol, and related compounds inhibit polymeriza-

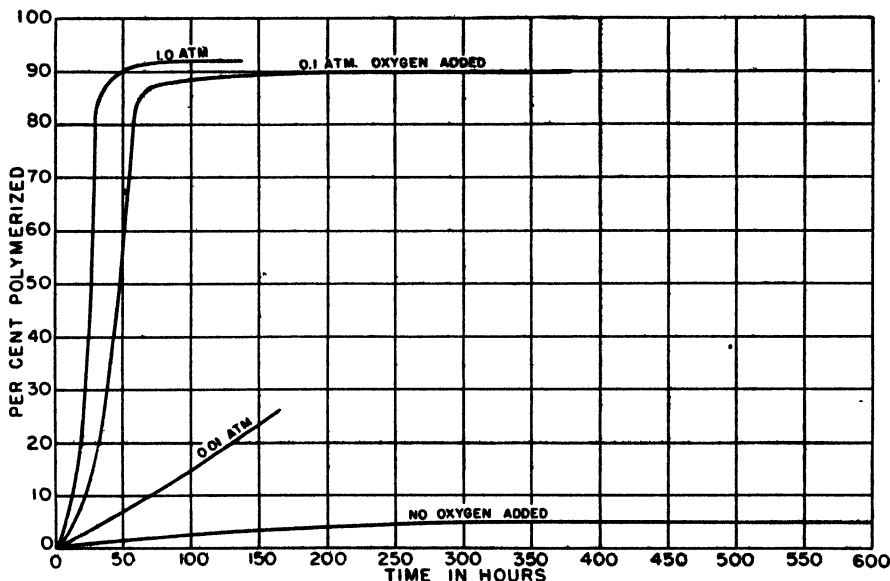


Figure 201. Effect of oxygen on the polymerization of methyl methacrylate at 65° in the dark. (Peroxides removed with triphenylmethyl. Methyl methacrylate distilled in absence of air and sealed in Pyrex tubes.) (*E. I. du Pont de Nemours & Co.**)

tion. The former, especially, is used for this purpose in commercial handling of the monomers. Oxygen-free methyl methacrylate, from which oxygen has been removed by means of triphenylmethyl, for example, does not polymerize appreciably in the dark at temperatures below 100°. At higher temperatures, polymerization occurs even in the absence of both light and oxygen. The catalytic effect of the latter at 65° is shown in Figure 201.

Oxygen in excess, however, may inhibit both photochemical and thermal polymerization of methyl methacrylate. Barnes has attempted to explain this behavior on the basis of the following reactions:

- (8) $M + UVL \longrightarrow M^*$
 (9) (a) $M^* + O_2 \longrightarrow MO_2$ (preferred reaction)
 (b) $M^* + M \longrightarrow MM^* + M \longrightarrow MMM^*$ etc.

Where oxygen is present in large excess, all activated monomeric molecules are at once consumed by formation of peroxide. According to this theory the erratic induction period behavior of various monomers in the presence of air can be explained as well as the formation of a soft or fluid layer at the surface of an otherwise hard mass of polymer—often found on polymerizing methyl methacrylate and other unsaturates in the presence of air. This surface effect is particularly significant industrially in the casting of certain cinctact resins (see Chapter 19).

The influence of heat and light, as well as of oxygen, on the rate of trially in the casting of certain contact resins (see Chapter 19).

Table 79. Effect of Oxygen, Heat, and Light on the Polymerization of Methyl Methacrylate⁶

Temperature (°C)	Oxygen Pressure (atm)	Time (hr) Required for Polymerization of		
		First 5%	First 25%	Second 25%
30	0.0	300	—	—
30	0.1	300	—	—
30	1.0	300	—	—
65	0.0	200	—	—
65	0.1	14	35	13
65	1.0	10	22	8
100	0.0	200	—	—
100	0.1	1	2.8	1.8
100	1.0	0.75	1.2	0.5
170	0.0	13	68	70
210	0.0	6	32	—
Light at 35	0.0	240	450	—
Light at 35	0.1	41	75	14
Light at 35	1.0	92	108	12

The effect of temperature and concentration of catalyst on the length of the induction period before polymerization begins and on the time required for 95 per cent polymerization is shown in Table 80.

Table 80. Effect of Temperature and Catalyst on Polymerization of Methyl Methacrylate⁶

(50 Volume Per Cent Methanol and Water)

Temp. (°C)	Time (hr)							
	0.0% Catalyst		0.1% Catalyst		0.5% Catalyst		1.0% Catalyst	
	Induction	Polymerization	Ind.	Polym.	Ind.	Polym.	Ind.	Polym.
65	50	70	4	10	1	4	0.5	2.5
80	0.6	3	0.2	1	0.1	0.5	0.1	0.3

The rate of polymerization of methyl methacrylate decreases as the solution of monomer becomes more dilute. Furthermore, the molecular

weight of the polymer decreases as reaction progresses. The influence of concentration on the rate of polymerization in benzene solution is shown in Figure 202.

Not only the rate of polymerization of acrylic esters but also the nature of the polymer depends on the temperature, the presence or absence of light, the nature and concentration of the catalyst, the nature and concentration of solvent employed, and the presence or absence of other

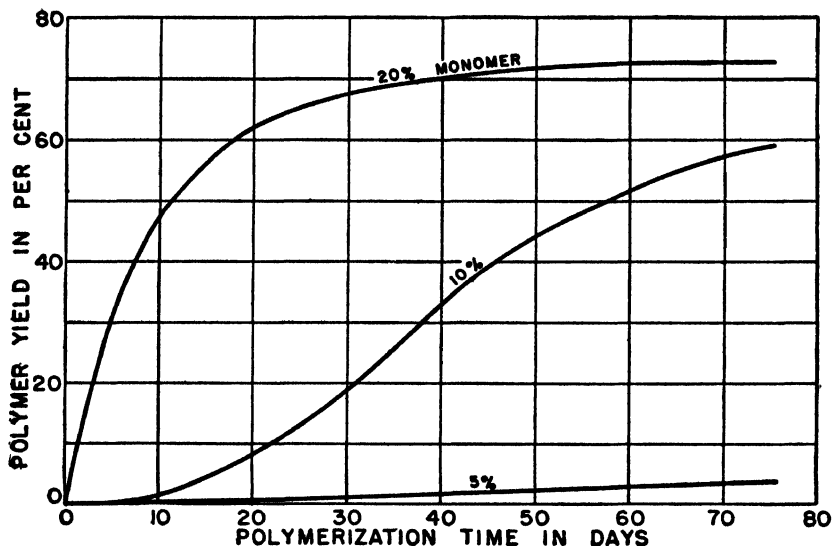


Figure 202. Rate of polymerization of methyl methacrylate in benzene solution at 65°. (*Strain*⁸⁵)

impurities. The effects of some of these factors on molecular weight and character of polyethyl acrylate are shown in Table 81.

In accordance with the rule which is generally applicable to addition polymerization, the more concentrated the solution of monomer in a given solvent, the higher is the molecular weight of the polymeric acrylate. Tables 81 and 82 both illustrate this fact.

The nature of the solvent exercises a specific effect on both the rate of polymerization and the molecular weight of the polymer, as shown in Table 83 and Figure 203.

As brought out by Table 81, the molecular weight of a polyacrylate is smaller, the higher the temperature at which polymerization is carried out. This effect is further illustrated by Figure 204, which likewise shows that the molecular weight of polymethyl methacrylate is smaller, the greater the concentration of catalyst used in forming it.

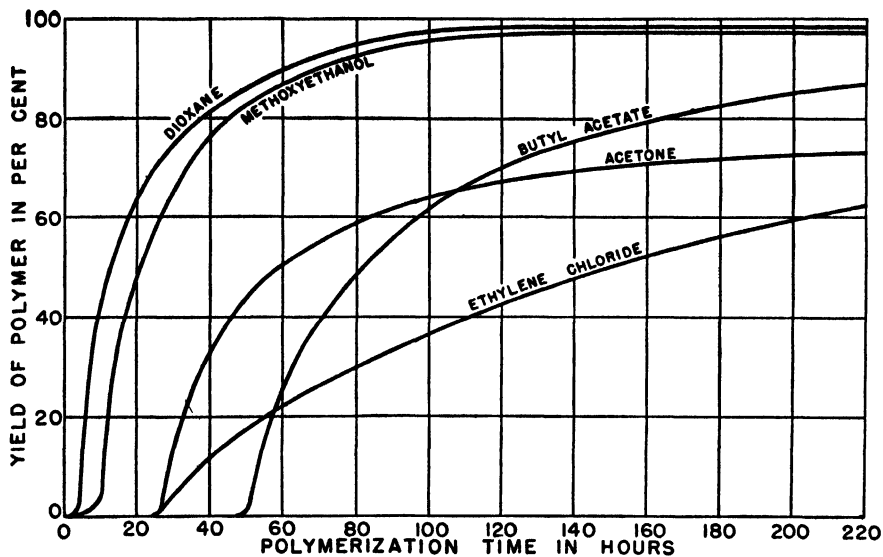


Figure 203. Rate of polymerization of methyl methacrylate at 65° in 20 per cent solution in various solvents. (Strain⁸⁵)

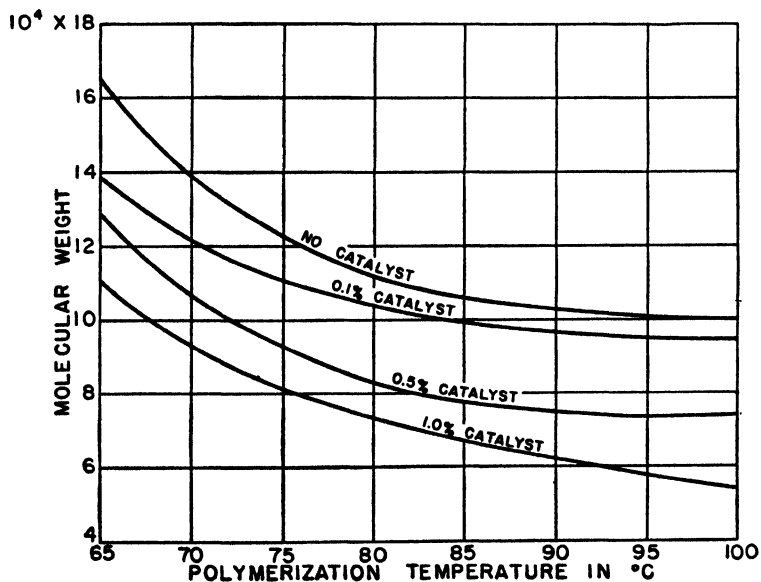


Figure 204. Variation of molecular weight of polymethyl methacrylate with temperature of polymerization and catalyst (benzoyl peroxide) concentration. (Strain⁸⁵)

Table 81. Effect of Various Conditions of Polymerization on the Molecular Weight of Polyethyl Acrylate *

Concentration of Monomer in Moles	Solvent	Temp. (° C)	Time of Heating (days)	Molecular Wt. (Estimated from viscosity measurements)	Degree of Polymerization	Chain Length (Å)	Solubility in Benzene	Appearance and Properties
1	Butyl acetate	190	4	2,200	22	55	Soluble without swelling	Very viscous oil. Colorless.
2	Butyl acetate	200	20	4,000	40	100	Same	Same. Somewhat more viscous.
1	Butyl acetate	100	25	7,800	78	200	Same	Very viscous, still fluid mass. Stringy. Adheres to glass.
2	Butyl acetate	100	25	14,500	145	360	Slight swelling, then solution	Same. Still thicker. Strong tendency to string out.
4	Butyl acetate	100	25	22,500	225	560	Same	Same. Adheres strongly to glass. Stringy.
6	Butyl acetate	100	19	41,000	405	1,000	First swelling, then solution	Extremely viscous. No longer fluid. Little or no tendency to string out. Adheres strongly to glass.
100% Monomer	None; 0.1 cc peroxide-containing ether added	100	12	175,000	1,750	4,000	Enormous swelling, then solution	Extremely viscous, elastic, rubber-like mass.
100% Monomer	—	100	12	Insoluble colloid	—	—	Swells to 50 times its volume, but remains insoluble	Same

Table 82. Concentration Effect on Methyl Methacrylate Polymerization ^{as}

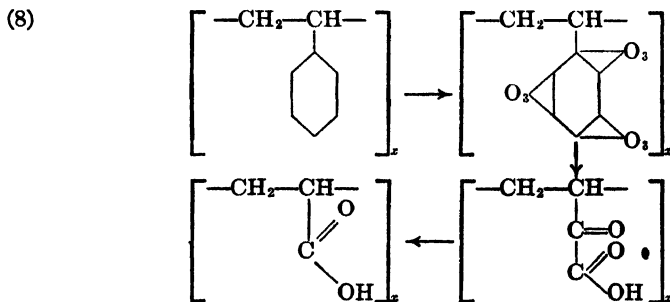
Monomer Concentration	In Methanol-Water Solution		Mol. Wt.	Monomer Concentration	In 95% Ethanol		In 95% Ethanol + 0.1% Catalyst	
	Induction Period	Yield			Induction Period	Yield	Monomer Concentration	Mol. Wt.
5%	45 hr.	—	100,000	20%	170 hr.	75,000	10%	35,000
10	21	—	140,000	30	140	77,000	20	36,000
20	18	—	168,000	50	96	90,000	30	43,000

Table 83. Polymerization Data for 20 Per Cent Methyl Methacrylate Solutions in Various Solvents ^{as}

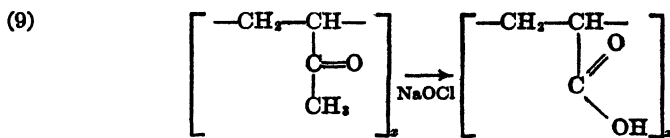
Solvent	% Yield		Mol. Wt. (in thousands)		Mol. Wt. (in thousands)		Mol. Wt. (in thousands)	
	24 hr	47 hr	72 hr	118 hr	225 hr	47 hr	118 hr	225 hr
Acetone	0	42	—	—	73	78.5	—	75
Dioxane	69	84	88	98	98	37	—	35
Ethylene chloride	0	16	25	42	63	75	—	54
Butyl acetate	0	0	40	69	86	—	—	41
Methoxyethanol	56	81	87	97	97	48	—	46
Methylene chloride	—	—	—	57	—	—	78	—
Ethyl acetate	—	—	—	70	—	—	58	—
95% ethanol	—	—	—	—	75	—	—	75
50% methanol + 50% water	—	90	—	—	—	166	—	—
Benzene	—	21	—	—	—	95	—	—

Polymerization of the acrylates can be carried out with or without solvent, in aqueous emulsion, or by granulation during temporary suspension of droplets of monomer in a non-solvent such as water. Other methods such as vapor-phase photochemical polymerization have been studied, but are not used commercially.

The Carbon Skeleton of Acrylate Resins. Several unique metathetical reactions have been carried out by Staudinger and his collaborators whereby these authors were able, for the first time, to convert a high polymer of a given series into one of a different type, thereby confirming the presence of a linear carbon chain in each. Polymeric esters of acrylic acid can be saponified with difficulty to yield polyacrylic acid. Moreover, although polyacrylic acid can be esterified directly only with difficulty, it can be transformed into polyethyl acrylate by reaction of its salts with ethyl iodide. In the case of hemicolloids, these metatheses occur without decrease in chain length of the polymer. In an entirely different series, long-continued action of ozone upon a carbon tetrachloride solution of polystyrene converts the latter into a mixture of di- and tri-ozonides. On boiling with water, the ozonides are hydrolyzed into soluble keto aldehydes and acids. On oxidation with concentrated nitric acid (which is without effect on polyacrylic acid) the reaction mixture is converted into a polybasic acid of high molecular weight, having the composition and properties of polyacrylic acid. This series of reactions is shown below.



Marvel and Levesque later obtained polyacrylic acid from a polymer of a still different type—polymethyl vinyl ketone—by oxidation with sodium hypochlorite:



General Properties of Acrylic Resins. The physical properties of the acrylic resins vary with the nature of the acid and alcohol used in the monomer and with their degree of polymerization. Methacrylates are harder than the corresponding acrylates. The higher the molecular weight of the alcohol component, the softer is the polymer, provided the chain is not branched. The greater the branching of the alkyl group, the higher is the softening point in a given group of isomeric polymers. Polymethyl acrylate is somewhat soft and rubber-like. Its films are tough and may exhibit as much as 1000 per cent extensibility before rupture. The lauryl derivative is a soft, tacky solid at room temperature. Polymeric

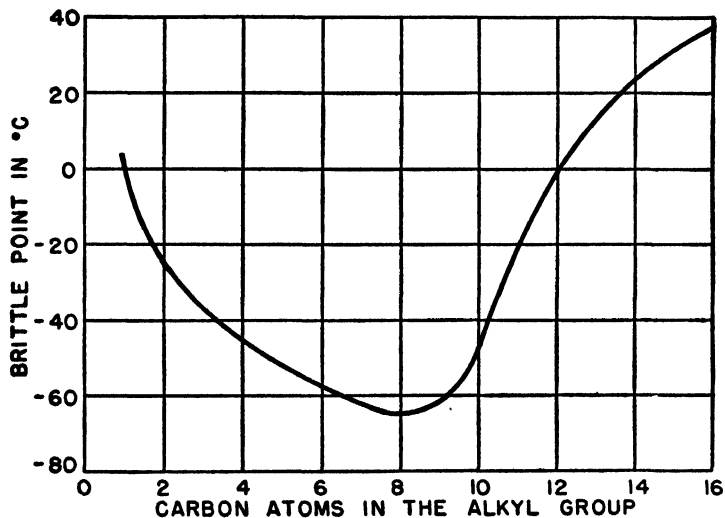


Figure 205. Brittle temperatures of the polymeric *n*-alkyl acrylates. (Rehberg and Fisher²⁸)

cetyl acrylate is a wax-like product which softens at about 35°. Other polymers fall between these limits. The relation between brittle point of polymers and the nature of the alkyl group of acrylic esters is shown in Figure 205. The effect of branching of the alkyl group is well illustrated by comparison of the four polybutyl acrylates. The normal derivative is soft and somewhat sticky. The isobutyl compound is harder and tougher, while the secondary butyl polymer is still harder, more nearly resembling the methyl ester. Finally, in polytertiary-butyl acrylate, pliability has almost completely disappeared. It is hard, tough, and somewhat brittle. It is the hardest of all the purely aliphatic acrylates. Cyclic esters, like cyclohexyl acrylate, give rise to hard, tough polymers.

The same generalizations apply to polymeric esters of methacrylic acid, as shown in Table 84.

Table 84. Properties of Methacrylate Esters⁶

Methacrylate	B.P. (°C)	Monomer (Mm)	Density at 20°	Softening temp. (°C)	Polymer. Molded Disc	Description
Methyl	100.3	760	0.945	125		Clear, hard, strong
Ethyl	116.5-117	760	—	65		Clear, tough
n-Propyl	141-143	765	0.921	38		Clear, tough, flexible
Isopropyl	125	760	0.888	95		Clear, strong
n-Butyl	51-52	11	0.894	33		Clear, flexible, strong
Isobutyl	46-47	13	0.884	70		Clear, slightly brittle
sec-Butyl	53-57	18	0.890	62		Clear, slightly brittle
tert-amyl	67-68	20	0.887	76		Clear, brittle
Diisopropyl carbonyl	72-75	9	0.876	60		Clear, very brittle
Octyl	105	5	—	< Room temp.		Clear, gel
Lauryl	142	4	—	< Room temp.		Clear, viscous liquid
Phenyl	83-84	4	1.053	120		Clear, very brittle
o-Cresyl	98-103	5	1.031	106		Clear, very brittle
Cyclohexyl	71-74	5	0.959	105		Clear, slightly brittle
p-Cyclohexyl phenyl	m.p. 67-68	—	—	145		Hazy, brittle, very hard
Furfuryl	80-82	5	1.055	78		Brown, hard, brittle
Tetrahydrofurfuryl	81-85	4	1.039	60		Transparent, brittle
β-Chloroethyl	61-64	11	1.106	68		Clear, colorless, tough
β-Phenylethyl	110-117	5	1.018	40		Clear, slightly brittle
β-Methoxyethyl	65-67	10	0.990	30		Clear, tough
β-Ethoxyethyl	91-93	35	0.996	< Room temp.		Clear, rubbery
ethylene glycol mono-	85-86	5	1.079	70		White, slightly brittle
ethylene glycol di-	83	2	—	—		Infusible, insoluble solid
α-Methyl allyl	57-59	15	0.921	—		Infusible, insoluble solid

A more detailed comparison of several physical properties of methyl, ethyl, *n*-propyl, *n*-butyl, and isobutyl methacrylate polymers appears in Table 35.

Table 35. Properties of Polymers of Various Methacrylic Esters^a

Property	Methyl	Ethyl	Normal Propyl	Normal Butyl	Isobutyl
Density—25°	1.19	1.11	1.06	1.05	1.02
Hardness (Pfund) ^a —g at 25°	220	141	100	1	210
Thermal yield point—°C	125	65	38	30	70
Tensile strength—lb/sq in	9,000	5,000	4,000	1,500	3,400
Impact strength (Dynstat) ^b —kg cm/cm ²	10.5	7.1	6.5	11.5	1.6
Refractive index	1.490	1.485	1.484	1.483	1.477
Extensibility—5 mil films (% at break)	4	7	5	230	2
Toughness ^c	98	174	76	1,000	23
Dielectric strength—volts/mil (thickness, 0.05 in)	740	—	650	625	—
Power factor—per cent at 25° and 60 cycles	6.5	—	3.8	6.2	—

^a Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 8th Ed., p. 300.

^b *Instruments*, 9, 218 (1936).

^c Area under load-elongation curves, expressed in arbitrary units.

Polymethacrylates become rubber-like above their softening point, but do not decompose below 200°. Above that temperature, gradual decomposition sets in. Between 350° and 450° nearly quantitative depolymerization can be carried out with very little carbonization. The monomeric ester thus obtained can be purified and reused if desired. Advantage is taken of this fact industrially in the depolymerization of polymer scrap by tossing it upon a bath of molten lead for regeneration of the monomer.

Mixtures of polymeric acrylates and methacrylates have not been found technically useful; in fact, the resins are often incompatible with each other. On the other hand, some control over properties can be exercised by copolymerizing various monomers.

In general, the greater the degree of polymerization of a given resin, the greater is its tensile strength and the more rapid is its recovery after extension.

Polymeric Esters of Acrylic Acid. Methacrylates have thus far proved of greatest technical importance and will be discussed in more detail in connection with commercial products. The acrylates are now receiving more attention than formerly. The preparation and properties of many acrylic esters have been described recently. Emulsion polymerization of acrylic esters has been discussed in detail in the chemical literature. Some of the emulsions thus prepared are sufficiently stable for application by dipping, brushing, spreading, or spraying. Ammonium persulfate is preferred as the catalyst for emulsion polymerization.

Benzoyl peroxide has been used to polymerize monomeric acrylic esters, and it is now known to function as a cross-linking agent at about 80° or higher when present in acrylic polymers. Cross-linked films can be prepared by spreading a solution containing polymethyl acrylate and benzoyl peroxide (2–5 per cent by the weight of polymer) on a suitable surface, allowing the solvent to evaporate, and then heating the resulting film at about 80° for 10 minutes or more.

Benzoyl peroxide, or preferably a mixture (such as "Lupercos" A) containing benzoyl peroxide, can be incorporated into polyethyl acrylate on a standard rubber mill. A soft, rubberlike material is obtained by heating.

Synthetic elastomers superior in certain respects to natural rubber can be made by vulcanizing polymers and some copolymers of ethyl acrylate. Although polyethyl acrylate can be vulcanized with benzoyl peroxide or quinone dioxime and red lead, the preferred method is to vulcanize a copolymer of 95 per cent ethyl acrylate and 5 per cent chloropropyl acrylate. The purpose of the chlorine, like unsaturation in natural rubber, is to facilitate vulcanization. The chlorine-containing copolymers have been vulcanized with (1) sulfur and certain accelerators, (2) quinone dioxime and red lead, (3) dinitrobenzene and litharge, (4) benzoyl peroxide, (5) "Polyac" (polymerized nitroso compound), and (6) certain amines such as triethylene tetramine or *p*-phenylene diamine which can function both as accelerators in the presence of sulfur, or as vulcanizing agents in their own right. Flex life and cut-growth resistance of the acrylic vulcanizates are outstanding, and in these properties acrylic vulcanizates are highly superior to GR-S synthetic rubber. Acrylic vulcanizates are equal to GR-S in milling characteristics, curing rate, available curing methods, tensile strength at normal temperatures, retention of tensile at 212° F, resilience at 212° F, and permanent set. Acrylic vulcanizates, designated as "Lactoprene" in the Eastern Regional Research Laboratory, are superior to GR-S in oil resistance, heat aging, resistance to oxidation and aging, and ease of preparation, storage, and processing.

Polymeric Acrylic Acids. Acrylic acid and methacrylic acid are both capable of polymerizing under suitable catalytic influence to yield hard materials which, depending on their molecular weight, either dissolve in water or only swell therein to rubber-like masses. Unlike polyacrylate esters, these products of high molecular weight are ionizable and, in aqueous and neutralized solutions, behave as heteropolar colloids, like the proteins. On addition of excess alkali (2N), their viscosity relations become normal, like those of homopolar high polymers.

Polymeric methacrylic acids are available commercially, but have not

yet found extensive use. It is reported that scratch- and heat-resistance of methacrylate resins are considerably improved by copolymerizing methacrylic acid or its anhydride with monomeric methacrylate esters.

COMMERCIAL PRODUCTS

Cast Shapes

Manufacture. The acrylics have achieved outstanding success in the form of cast sheets, rods, and tubes. Polymethyl methacrylate and copolymers of methyl methacrylate and ethyl acrylate are commercial representatives of this class. Domestic methacrylates are sold under the trade-marks "Lucite" and "Plexiglas," the former being that of du Pont, and the latter that of Rohm and Haas.

Polymerization of methyl methacrylate monomer is accompanied by evolution of heat and shrinkage, both of which are obstacles to the preparation of castings free from flaws.

The heat which is developed by polymerization tends to accelerate the reaction and thus gives rise to the production of more heat; consequently, the reaction tends to run away. If the temperature developed within the mass exceeds the boiling point of the monomer, the casting is marred by bubbles. The fact that the material is a poor conductor of heat contributes to difficulties of avoiding overheating of the center of any mass and makes this difficulty greater, the greater the minimum dimension of the mass.

Shrinkage of more than 20 per cent during conversion of monomer to polymer must be guided in the proper direction in order to prevent development of objectionable voids when this shrinkage is allowed to take place in random manner.

Early in the work with methyl methacrylate, several methods were developed for preventing the formation of bubbles. It was found that control of reaction was facilitated if the vessel containing the material undergoing polymerization was surrounded by a liquid of high specific heat (*e.g.*, water) instead of air. This liquid serves initially to impart to the vessel the heat required to start polymerization and then, by virtue of its large heat-capacity, to abstract excess heat from the vessel. Another method of checking reaction in order to prevent it from getting out of control comprises alternate heating to initiate or promote polymerization and cooling to check it again. Another procedure, which prevents the development of bubbles and also controls shrinkage by limiting it to the vertical dimension, is that of pouring and polymerizing successive layers. This process has the disadvantage of consuming considerable time.

Formation of bubbles in masses of methyl methacrylate during polymerization can be suppressed by application of pressure sufficient to prevent volatilization of the monomer. Application of pressure in some cases suffices also to prevent random shrinkage of the mass by keeping it at all times squeezed out into contact with the vertical walls of the container, thus confining all shrinkage to the vertical dimension.

In various processes of making shapes of methyl methacrylate resin by casting, it is found advantageous to cast a "syrup" rather than monomer. Syrups are prepared by partially polymerizing the monomer to form a viscous but pourable liquid. There are several advantages in using syrup instead of monomer; namely:

(1) Monomer does not begin to polymerize appreciably until after a certain "induction period," and this period is of different lengths with different lots of monomer. Time in the mold is saved by starting with syrup, which proceeds promptly to polymerize and which already contains some polymer.

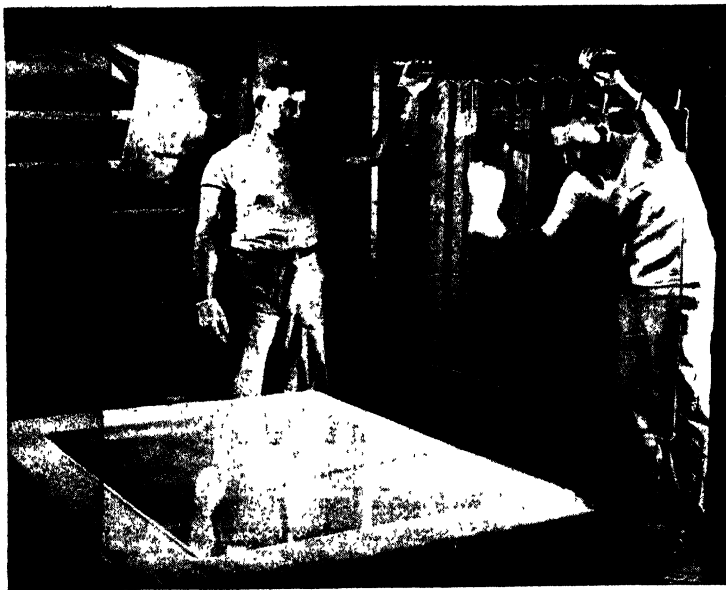
(2) Viscosity of the syrup reduces problems of leakage of equipment.

(3) A minor advantage lies in the fact that because some polymerization has already been accomplished in the syrup, the shrinkage in volume from syrup to polymer is slightly less than from monomer to polymer.

When plasticizer is used, its presence also reduces slightly the amount of shrinkage.

Cast sheets are produced by assembling two highly polished glass plates in parallel position, separated by means of a continuous rubber tube or solid strip running around their periphery. The compressibility of this rubber separator assures constant contact of the smooth glass surfaces against the resin as shrinkage progresses during polymerization. The rubber is wrapped in cellophane to protect it from contact with monomer. The glass plates are clamped lightly together and partially polymerized methyl methacrylate, with or without plasticizer, and containing a peroxide catalyst, usually benzoyl peroxide, is run into the cell. The open ends of the rubber separator strips are lapped and the assembly is then turned over into a horizontal position, with care to free the contents from any occluded bubbles. The unit is subsequently allowed to stand at an elevated temperature until polymerization is complete. The glass plates and separator strip are then removed and the sheet of plastic, which has acquired the high polish of the glass surfaces, is at once protected from scratching by covering it on both sides with a pressure-sensitive adhesive paper. The latter is retained as a covering until service requirements dictate its removal. At that time it can be readily stripped clean, rolled, and stacked for re-use if desired.

Gum rubber was formerly employed as an adhesive on this masking paper. During World War II, a synthetic substitute was developed. Moreover, protective sprays have been evolved which can be applied without injury to shaped methacrylate enclosures and which can subsequently be washed off with water. Because of the ease with which polymethyl methacrylate is scratched and because of the fact that most of its applications are optical, careful handling of this plastic to prevent scratches is a serious and important precaution which must be painstakingly



Courtesy E. I. du Pont de Nemours & Co.

Figure 206. Inspection of cast "Lucite" sheeting.

ingly observed in manufacture as well as in later shaping and fabricating operations.

Methacrylate rods are cast by means of an ingenious procedure covered by United States patent 2,057,674. During the casting process, the mass becomes fairly rigid before polymerization is finished and hence before shrinkage has ceased. If polymerization is proceeding to completion simultaneously in all parts of the mold, pressure alone will not suffice to control shrinkage in a mold of considerable vertical depth, such as that required for making long rods. In this so-called immersion method, polymerization is caused to begin at the bottom of the mold and proceed gradually upward. At any one time, polymerization is going on actively only in a relatively shallow zone, while the material above this

zone is maintained in a liquid condition to insure transmittal to the zone of polymerization of the pressure required to prevent horizontal shrinkage. Gradual raising of the zone of polymerization is accomplished by correspondingly gradual immersion of the mold in hot water, and the depth of the zone of polymerization is restricted by directing a blast of cold air on the mold above the water level.

In practice, aluminum tubes of uniform bore serve as molds. These tubes are fastened into circular headers, top and bottom, the number of tubes varying with the size of rod to be cast. In the case of $\frac{3}{8}$ -inch rod, there may be as many as 500; in the case of 2-inch rod as few as 20. The central section of this multi-rod mold is left free for an air blast and water spray to enter at the top. Both top and bottom headers are sealed by means of solid plates of the same diameter. The multi-rod mold, in a vertical position, is lowered into a vat the bottom of which is covered with hot water. The water level in the vat can be adjusted by raising or lowering the elbow of a curved exterior hose attached to the bottom of the tank and elevated automatically with a screw mechanism. The surface of the hot water inside the tank is covered with a floating plug in the central portion and with a layer of wax elsewhere. This protection keeps down steam from the water, which may be raised to a temperature of 190° F, and acts as a barrier between the lower hot zone where polymerization occurs and the upper cold zone where the syrup must be kept fluid so that it will fill the aluminum tube as shrinkage occurs during resinification.

Partially polymerized methyl methacrylate containing some 10 per cent of dibutyl or diamyl phthalate as plasticizer and the requisite quantity of benzoyl peroxide is run into the tubes. Throughout polymerization, direct connection of the tubes, through the top header, is maintained with a refrigerated reservoir of partially polymerized syrup which is forced into the mold under moderate pressure by means of a bellows-type pump free from moving parts which might become abraded and contaminate the resin.

During polymerization, a blast of cool air and a water spray is sent down the central main. The water level is slowly raised during polymerization, which requires some four to six hours for $\frac{3}{8}$ -inch rod, approximately four feet in length, and ranges upward to about twenty-four hours for 2-inch rod of the same length. By thus maintaining a cooled zone above the wax floating on the water, and a hot zone below it, polymerization of methacrylate inside of the tubes is made to progress upward gradually as the hot water level rises. The material inside of the tubes above this level is thereby held in a liquid state and the tubes are continuously kept full of syrup entering at the top under pressure.

After completion of polymerization, the mold is raised from the vat and cooled, and the rods are removed mechanically. Because the plastic possesses a greater coefficient of thermal expansion than aluminum, sufficient shrinkage away from the metal occurs during cooling to permit removal. This differential shrinkage amounts to between two and three thousandths of an inch in the case of $\frac{3}{8}$ -inch rods. Below this diameter, removal is impractical, and hence recourse is had to extrusion for smaller rods.

Rods having a mother-of-pearl effect, especially favored for fabrication of beads and other jewelry, are produced by mixing "pearl essence" with the methacrylate syrup before polymerization. "Pearl essence" is a resinous dispersion of minute fish scales.

Cast tubes are manufactured by centrifugal methods whereby the polymerizing fluid is distributed in uniform thickness over the interior walls of closed aluminum tubes rotating on a horizontal axis at 200 to 300 rpm and heated by means of a hot water spray. Partially polymerized methacrylate syrup is used in this instance, also, although the extent of permissible polymerization is less than in the case of rods and sheets. Miscellaneous cast objects can be produced from methyl methacrylate by observing precautions so that the mold will be maintained full as polymerization progresses. As will be mentioned later, botanical or zoological specimens may be imbedded in polyethyl methacrylate by using casting technique.

Properties. Most of the applications of cast methacrylates are attributable to their unique optical properties. They possess a degree of transparency rivalled by no other plastic and excelled by no other substance. All wave lengths of visible light, *i.e.*, from 3600 to 7200 Ångström units, are transmitted, the percentage transmission being 90 to 92, while the optical density is about 0.036. Permanence of transparency is excellent. After 700 calendar days of exposure at 40° N. latitude, comprising 200 full sunshine days, it has been found, for example, that the transmission of white light by a $\frac{1}{4}$ -inch sheet of methacrylate sheeting decreases only 1 per cent, with no appearance of haze. After 2000 hours of exposure in an Atlas Fade-ometer, a slight haze appears, with eight per cent decrease in transmission of white light. Decrease in transmission of blue light is somewhat greater and is more pronounced as the wave lengths become shorter. This effect is known as solarization. Transmission of ultraviolet is shown in Figure 207 and is there compared with transmissivities of other transparent substances. On continued exposure, ultraviolet transmission decreases until it reaches an approximately constant value after two or three months, at which time fluorescence becomes apparent. Sheets of $\frac{1}{4}$ -inch thickness, for example, having an

initial ultraviolet transmission of 76 per cent, decrease in transparency to about 50 per cent. The absorption of x-rays by polymethyl methacrylate is comparable to their absorption by human flesh.

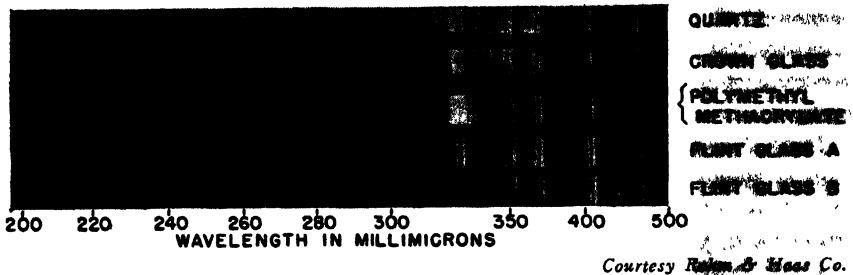


Figure 207. Comparison of the ultra-violet transmission of polymethyl methacrylate ("Plexiglas") with some inorganic transparents.

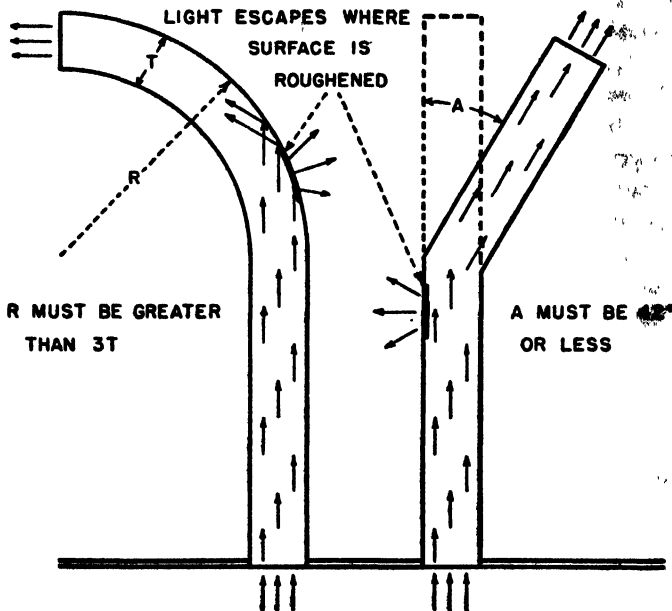


Figure 208 Limits of angle of bending and radius of curvature for conduction of light through rods of polymethyl methacrylate.

The perfect clearness of methyl methacrylate resin and its ability to take a high polish make it useful in optical and illuminating devices based on total reflection of light. If a smooth-surfaced rod or sheet of

resin is curved on a radius large enough so that a beam of light entering it axially makes with the curved surface an angle of which the tangent is not larger than the index of refraction of the resin, the light is totally reflected within the rod, and the rod will carry light around a corner in the manner illustrated diagrammatically in Figure 208. In the case of an angular bend, the deviation from 180° should be 42° or less, curves should not be formed to an outer radius of less than three times the thickness of the sheet or the diameter of the rod.

No light is visible from within the rod, because the resin, being completely clear, contains no foreign particles which would divert the light from its path within the rod and cause it to escape by impinging upon the surface at an angle larger than the limiting one.

Light can, however, be caused to escape at predetermined areas of the surface by roughening these areas by sanding or engraving, so as to produce surfaces at such angles that light impinges upon them at greater than the limiting angle. This method of producing illuminated areas is used in making edge-lighted signs, instrument panels, surgical instruments, and other devices.

A serious drawback of the methacrylate resins which has prevented more general application where a transparent shatterproof material is desired lies in their lack of abrasion-resistance. To some extent this property is a function of hardness, but it is also dependent upon other properties such as elastic modulus, toughness, and heat-resistance. Cast methacrylates show a Brinell hardness of 18 to 23 (500 kg, 10 mm ball), a Rockwell M hardness of about 94, a Rockwell H hardness of about 60, and a Vickers hardness of 18 to 20. On Mohs' scale they lie between gypsum and calcite, having a value of 2 to 3. They will scratch aluminum, copper, and tin. The Bierbaum number of cast methacrylate is from 15 to 18.

Recent developments in cast as well as molded methacrylates have resulted in substantial improvement of surface hardness. Products are at present available in limited amounts. They are partially crosslinked by copolymerization of a small amount of a doubly unsaturated monomer, such as methacrylic anhydride, with methyl methacrylate. These resins also possess greater heat-resistance and are less readily shaped than the linear methacrylates already described.

Because of the fact that the methacrylates are thermoplastic, they soften at sufficiently low temperatures to permit shaping. On the other hand, because of their thermoplasticity, it is necessary to adjust the design of tools and speed of machining so that the plastic will not ball up. Under proper operating conditions, methacrylates can be readily

sawed, drilled, threaded, tapped, and otherwise machined. As with most plastics, the thermal coefficient of linear expansion of cast methacrylates increases with rising temperature, as shown in Table 86.

Table 86. Linear Coefficient of Thermal Expansion of Cast "Lucite" Sheets¹

Temperature Range (°C)	Linear Coefficient of Thermal Expansion per °C $\times 10^{-4}$
- 75 to \pm 0	6.4
\pm 0 to + 25	8.2
+ 25 to + 50	9.4

After attaining equilibrium under normal atmospheric conditions, methacrylates contain approximately 0.5 per cent of moisture. On long continued exposure of these resins to water at temperatures up to about 60°, they reach an equilibrium after absorption of about 1.5 per cent of water by weight. They are resistant to attack by water and dilute aqueous solutions of most chemicals, including acids and bases, aqua regia excepted. They are unaffected by aliphatic hydrocarbons, fatty oils, glycerol, and glycol. Specific solvents include acetone, trichloroethane, chloroform, ethylene dichloride, furfural, and toluene. In general, the methacrylates are more or less readily attacked by many alcohols, esters, ketones, aromatic hydrocarbons, chlorinated solvents, phenols, carbon disulfide, and lead tetraethyl.

Because of their extensive use in airplane windscreens, the strength characteristics of the methacrylates under varying weather conditions are important. Although moisture does not exercise much influence on these properties, temperature often does. Tensile strength of the methacrylates increases rapidly as the temperature drops. This effect is brought out for "Lucite" in Figure 209.

The effect of the rate of loading is equally marked; the more slowly the load is applied, the lower is the tensile strength. This situation can be attributed to fatigue, a factor of utmost importance in engineering applications of plastics, especially where vibrations are encountered as, for example, in airplane windscreens.

According to the manufacturer,¹ "Long-time tension tests, in which the test bar supports a dead weight, indicate that 'Lucite' will not withstand indefinitely a tensile stress greater than one-half the amount which is given on the stress-strain curve as the breaking load when measured at a testing speed of 0.05 inch per minute. The stress-strain graph, Figure 209, can thus be used to obtain approximate values from the breaking load given at each temperature. Thus, at 68° F, the breaking load is 8,000 pounds, indicating a fatigue tensile strength of 4,000 pounds per square inch. Allowing the conventional factor of safety of two, the

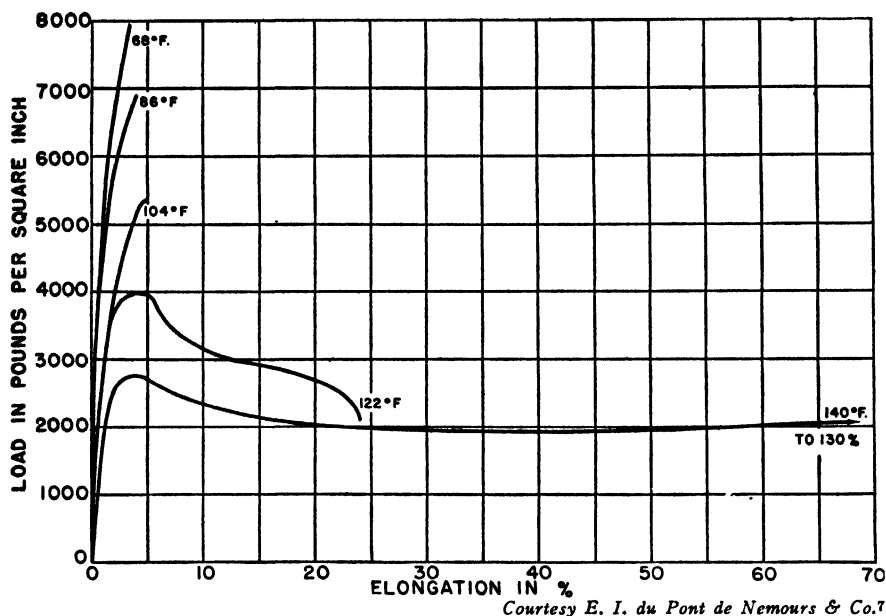


Figure 209. Stress-strain curves for cast "Lucite" at different temperatures under low testing speed. (ASTM D229-39T. No load cross-head speed: 0.05 inch/min.)

operating tensile strength is then 2,000 pounds per square inch. Design based upon a fiber stress of 2,000 pounds per square inch, however, makes no allowance for a decrease in tensile strength with a rise in temperature. Furthermore, the desirable optical properties of cast 'Lucite' may be lost by 'crazing,' *i.e.*, the development of a network of tiny cracks which appear when transparent plastics are subjected to excessive fiber stress. For these reasons, the design of members subjected to continued loads should avoid fiber stresses in excess of 1,000 pounds per square inch for temperatures below 77° F. From 77° to 100° F a maximum operating fiber stress of 650 pounds per square inch is recommended."

Another factor affecting tensile strength of cast methacrylate sheets is the nature of the shaping operations. A limited degree of molecular orientation may be caused by various shaping procedures, resulting in an increase of strength in one direction attended by a decrease in the direction at right angles thereto. Sharp bends, machine marks, scratches, or other surface irregularities will also result in impairment of tensile strength.

Unlike tensile, compressive, and flexural strengths, the impact strength of polymethyl methacrylate is scarcely affected by temperatures ranging

Table 87. General Properties of "Lucite" *

Property	Cast "Lucite" General Purpose	Molded, "Lucite"
Mechanical		
tensile strength—psi	6,000–9,000	5,000–10,000
modulus of elasticity in tension—psi	$3-5 \times 10^5$	$3-5 \times 10^5$
elongation—%	1–5	1–5
compressive strength—psi	10,000–12,500	10,000–15,000
flexural strength—psi	10,000–14,000	9,000–15,000
impact strength, Charpy—ft-lb per in of notch	0.4–0.6	0.4–0.6
Isod—ft-lb per in of notch	0.2–0.4	
hardness, Rockwell (load removed within 1 sec after fully applied, reading 30 sec later)	M94	
Thermal		
coefficient of linear expansion—per °C (0°–21°)	$7-9 \times 10^{-5}$	$7-9 \times 10^{-5}$
thermal conductivity—cal per cm ² per sec per °C per cm	$5-8 \times 10^{-4}$	$5-8 \times 10^{-4}$
Btu per sq ft per hr per °F per in	1.5–2.3	1.5–2.3
softening temperature—°C (cantilever beam)	86	80–104
specific heat—cal per °C per g (0–21° C)	0.35	0.35
Optical		
index of refraction— <i>n_D</i>	1.496	1.49–1.51
mean dispersion	0.0085	
dispersive power	0.0174	
light transmission—% (visible range, uncorrected for reflection)	90–92	90–92
Electrical		
volume resistivity—ohm-cm	greater than 10^{15}	greater than 10^{15}
dielectric constant, 60 cycles	4.5	3.6–3.8
10 ³ cycles	3.2	3.0
10 ⁶ cycles	2.7	2.8
power factor—%, 60 cycles	5.0	7.0
10 ³ cycles	4.4	7.0
10 ⁶ cycles	1.5	1.5
dielectric strength, short time—v per mil	400	400
step-by-step—v per mil	350	300
unpigmented stock ($\frac{1}{8}$ -inch sample) will not track on arcing		

Molding

compression ratio	1.7-2.2
molding temperature—° F, compression injection	280-350 325-475
molding pressure-psi, compression injection	2,000-7,500 10,000-35,000
mold shrinkage, cold mold to cold piece—in per in, compression injection	0.003-0.005 0.003-0.006

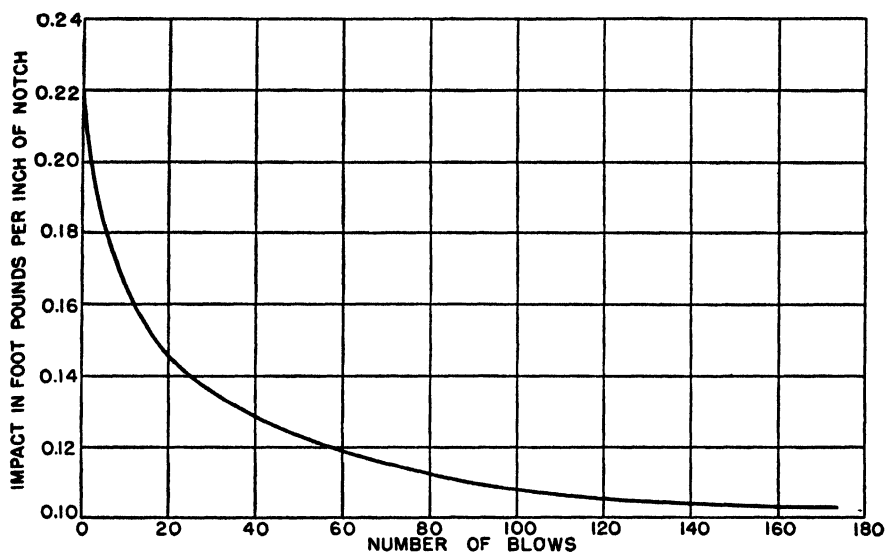
Miscellaneous

specific gravity	1.18-1.20
specific volume—cu in per lb	24-23
water absorption—% by wt, 24 hr immersion	0.3-0.4
tendency to cold flow	slight
burning rate (in/min)($\frac{1}{2}$ in thickness)	1-2
effect of age	practically none
effect of sunlight	practically none
effect of metal inserts	none
chemical resistance	Unaffected by weak acids, weak alkalies; attacked by strong acids and strong alkalies. Soluble in lower ketones, esters.

“Lucite” is transparent and crystal-clear. Unlimited transparent, translucent and opaque colors can be made. It is easily machined and can be formed into intricate shapes at temperatures ranging from 248° to 300° F.

* Manufacturers' data. E. I. du Pont de Nemours and Company, Inc.

from -60 to $+80^{\circ}$. Water-absorption exercises relatively little influence on any of the strength characteristics of this plastic; such an effect is most marked in the case of tensile strength where reduction of a few per cent may at times be encountered. Factors influencing impact strength include molecular orientation, surface irregularities, and fatigue.



Courtesy E. I. du Pont de Nemours & Co.

Figure 210. Fatigue endurance of cast "Lucite" under repeated impact as determined by the Bell Telephone Laboratories falling ball method.

The impact resistance of "Lucite," for example, may decrease from 40 to 60 per cent of its original value under repeated shock. This fact is shown strikingly in Figure 210.

Various physical properties of the methacrylates are summarized in Tables 87 and 88, which give characteristic values for "Lucite" and "Plexiglas," respectively.

Table 88. Properties of "Plexiglas" *

Since "Plexiglas" is a thermoplastic, its properties will be found to vary with the temperature of the material. The values given apply for 25 to 30°C (77 to 86°F)

Optical Properties

Clarity	
Light transmission	91-92%
Scattering effect	Practically nil
Refractive Index n_D	1.488-1.489
Dispersion	0.008

Physical Properties

Specific gravity	1.18-1.19
Hardness	
Mohs	2-3
Vickers	18-20
Brinell	18-20 (500 kg, 10 mm ball)
Tensile strength	7,000-9,000 lb/sq in
(Elongation at failure)	5-15 %
Flexural strength	14,000-16,000 lb/sq in
Compressive strength	11,000-13,000 lb/sq in
Impact resistance	0.3-0.5 ft lb (A.S.T.M. Charpy notched bar)
Modulus of elasticity	4-6 $\times 10^5$ lb/sq in
Coefficient of expansion	8 $\times 10^{-5}$ /° C
Water absorption by weight	
24 hr	0.3 %
48 hr	0.4 %
500 hr	1.2 % (equilibrium)

Electrical Properties

Dielectric constant (60 cycles)	3.4 to 3.6
(1,000,000 cycles)	3.2
Power factor (at 60 cycles)	5 to 6 %
Volume resistance	10 ¹⁵ ohms/cm*
Dielectric strength (short time test)	500 volts/mil
(one minute stepwise)	400 volts/mil

* Manufacturers' data. Rohm and Haas Company

Applications. Cast methacrylates have found numerous applications, the most important being as transparent airplane enclosures. Because of their excellent optical properties, their low density, their resistance to weathering, and their retention of impact resistance at low temperatures, these plastics are well suited to this use and were employed on every combat plane during World War II. Two- and three-dimensional noses, gun-turrets, blisters, tail-pieces, and other enclosures are formed from cast methacrylate sheets, sometimes reinforced with methacrylate ribs. Production of cast sheets for aviation uses increased eight-fold from 1940 to 1942 and steadily continued to multiply during World War II.

Shaping is carried out at temperatures between 245 and 310° F. Because of the elastic memory of this plastic, shaped sheets tend to revert to their initial form when reheated to a sufficiently high temperature, but this unloading does not occur in service, even at temperatures of equatorial deserts. Great care must be exercised during shaping to prevent scratching.

In mounting methacrylate sections on planes, concentrations of stress should be avoided. Channel mounting is preferable to bolting or riveting. It is essential to cushion the plastic where it touches the metal re-



Courtesy E. I. du Pont de Nemours & Co.

Figure 211. Single sheets of "Lucite," trimmed to approximately oval shape, are heated in ovens to the point where the thermoplastic material becomes flexible, as the first step in the process of shaping enclosures for the P-51 Mustang fighter planes by the vacuum-drawing method which preserves the superior optical qualities of the plastic unimpaired.



Courtesy E. I. du Pont de Nemours & Co.

Figure 212. Operator applies the vacuum which shapes "Lucite" sheet into an enclosure for the P-51 Mustang fighter planes by the vacuum-drawing method.



Figure 213. Enclosure for the P-51 Mustang fighter plane made of "Lucite" is removed from vacuum die in which it has been shaped to specified dimensions.

Courtesy E. I. du Pont de Nemours & Co.



Courtesy Rohm & Haas Co.

Figure 214. Upper turret gunner on a B-25 Mitchell has the "bird's eye" view on combat missions. His manually-controlled, electrically operated turret with its "Plexiglas" enclosure swings around in a 360° circle, enabling him to see any direction from zenith to his horizon. He takes aim through his optical gun sight to fire his twin .50 caliber machine guns. Armor plate at the back of the "Plexiglas" enclosure protects his head, as shown in this photograph.

tainer. This precaution must be observed to preclude the possibility of crazing. Numerous methods of mounting have been worked out in great detail by the manufacturers of these plastics.

The lack of scratch-resistance is the greatest shortcoming of the methacrylates and would prevent their use in automobile windshields. In airplanes this weakness is not as serious as in vehicles moving on the ground. Nevertheless, airplane enclosures do get scratched and must often be polished in service. Methods of accomplishing this operation, as well as means of stopping cracks and patching bullet holes, both temporarily and permanently, have also been developed with great care because of their military importance. Comprehensive literature on shaping, mounting, polishing, and repairing is available from the manufacturers of these plastics, who have also cooperated with the Army Air Forces in producing a film for aircraft training schools which shows proper methods of polishing and repairing airplane enclosures.

Methacrylate sheets have been used also in tank sight windows, while naval PT boats have been equipped with methacrylate windows and machine-gun housings.

Laminated windows comprising a sandwich of two methacrylate sheets and a polyvinyl butyral interlayer, developed for greater safety in military applications, have been discussed in Chapter 14. Such sandwiches are used as enclosures on planes with pressurized interiors for flight at high altitudes. The tough interlayer minimizes shattering around bullet-holes and is to some degree self-sealing. Thus a measure of protection is provided against loss of pressure resulting from perforation of the enclosure.

A great diversity of other uses in military, industrial, and consumer goods have been developed for cast methacrylates. A partial list of such applications includes housings for marine-engine water-filters, draft gauges, edge-lighted instrument panels, edge-lighted pointers and signs, curved dental, surgical, and industrial instruments for piping cool light to difficultly accessible locations, machine windows and guards, transparent models, optical equipment, scientific instruments such as transparent dialysers, beer-tank gauges, furniture, traffic-directors, display fixtures, edge- or end-lighted carved murals, decorative columns, and rails, and such miscellaneous novelties as handbag frames, pipe-stems and racks, cigarette boxes, trays, costume jewelry, brush-backs and handles, compacts, lamps, frames for mirrors and pictures, and transparent "stunt" row boats.

Most applications of cast methacrylates utilize colorless stock. A few uses, especially beads, bracelets, and other articles of costume jewelry, require the much more costly stock containing pearl essence discussed in

the preceding section. Cast sheets, rods, and tubes can also be made in a number of transparent, translucent, and opaque colors where volume justifies production. In their manufacture, a soluble dye or insoluble pigment is diffused throughout the material prior to casting. Cast shapes may be dip-dyed, in which case the dye is deposited on or near the surface. Various oil-soluble dyes dissolved in aqueous acetone may be used in this manner. It is often desirable to paint one surface of a methacrylate object. Numerous paints and lacquers may be used for this purpose, but those containing volatile solvents capable of attacking the surface of the plastic should be avoided. In general, aliphatic hydrocarbon solvents should be preferred.

Cementing operations need frequently to be carried out with methacrylates. Any one of three general methods can be used:

(1) Surfaces to be joined may be softened with a suitable solvent such as ethylene dichloride or glacial acetic acid and the softened areas then united and held in position until a firm union is established. Solvent should be allowed to evaporate completely before further machining operations are carried out.

(2) The joint may be established by coating both surfaces with a solution of polymethyl methacrylate in ethylene dichloride, ethyl acetate, or other suitable solvent.

(3) Polymethyl methacrylate may be dissolved in the monomer, to which a small amount of peroxide catalyst is added, or catalyst may be added to the monomer alone which is allowed to stand until partial polymerization has occurred. The paste is then used to establish a bond which hardens through polymerization of solvent monomer, rather than by evaporation.

In all cementing work, it is practically impossible to produce an optically perfect joint. A bond having good mechanical properties, however, can be made by exercising extreme care in preparation of the mating surfaces and in application of the cement so as to avoid bubbles, voids, and contamination.

Available Shapes. Cast methacrylates are available under the trademark names "Lucite" and "Plexiglas." Sheets are manufactured regularly in thicknesses of 0.060 to 0.500 inch. Cast sheets up to 2½ inches thick are produced for special applications. In lots of 50 sq ft or more, the 1946 price per sq ft for the first size mentioned was \$0.75. Weight per sq ft, for the same size is 0.36+ lb.

Cast rods are available in diameters up to 2 inches in 48-inch lengths. The price of rods ranges from about \$1.25 to \$1.50 per pound, depending on size.

Tubes are manufactured in various wall thicknesses and diameters.

Special forms can be obtained upon demand, as well as shaped sheets.

Special Products. During World War II, the Polaroid Corporation developed polycyclohexyl methacrylate (CHM) for casting high-precision optics.

Molding Powders

Polymethyl methacrylate is available under the trade names "Lucite" and "Plexiglas" (formerly "Crystalite") in the form of molding powder in both colorless and colored varieties. These powders are often produced by granulation methods of polymerization. Colors or pigments may be admixed at the time of granulation, but they are commonly added later on rubber rolls. Various copolymers, including those of



Figure 215. Molded "Lucite" sheet being removed from the press.

Courtesy E. I. du Pont de Nemours & Co.

methyl methacrylate and styrene have been patented as molding materials.

Molded sheets are available in standard 20×25 inch size from $\frac{1}{8}$ to 2 inches thick. The clarity and uniformity of molded sheets is usually slightly inferior to that of cast sheets. Extruded rod and tubing is also manufactured.

Because of the thermoplastic character of these resins, they are usually injection-molded, temperatures ranging from 325 to 475° F and pressures from 10,000 to 35,000 pounds per square inch. Compression molding is carried out, where necessary, at lower temperatures and pressures.

In general, properties of molded methacrylates are similar to those of the cast resins. Comparative properties of cast and molded "Lucite" have been listed in Table 87.

Applications of molded methacrylates are many and varied. Most of

them depend on their unique optical properties. Some, like fruit-juicer parts, have resulted from the combination of good mechanical properties and corrosion-resistance. Miscellaneous uses of molded methacrylates include automobile dashboard panels, instrument dials, knobs, and radiator ornaments, reflectors and blackout lenses for military vehicles, flares, airport signal-light lenses, and retro-directive highway reflectors. The last application is particularly striking inasmuch as a unique mold design permits unusual accuracy in molding the highly polished cubical facets on the rear of the reflector which cause efficient reflection of light impinging upon these road markers from the headlights of approaching vehicles. Use of these "Stimsonite" molded methacrylate reflectors has greatly reduced night driving accidents upon main highways along which they have been installed. Other methacrylate uses include gas-mask lenses, instrument lenses, and numerous surgical and medical applications such as arthritic hip reliner cups, contact optical lenses (now worn by about 5,000 people and potentially of vast adaptability), jaw and knuckle joints (as a substitute for metal plates in bone grafting), "cold light-piping" instruments—including tongue depressors, cystoscopes, sigmoidoscopes, proctoscopes, otoscopes, pharyngoscopes, brain and tonsil probes, and speculums—shields to protect doctors who are treating infectious diseases, windows in plaster casts, stethoscope parts, transfusion tubes, incubator covers, and drainage tubes. Still other applications include camera view-finder lenses, magnifying glasses, watch crystals, shatterproof spectacle lenses, hearing aids, transparent containers and instrument cases, antenna housings, housings for electric water lights on life-preservers and life-rafts, nameplates for vacuum cleaners and other devices, Venturi tube parts on airplanes, oxygen flowmeter parts, oil cups and various types of lubricating equipment, insulation for radio equipment, neutralizing condensers, illuminated transparent typewriter rolls for stencil-cutting, hair-dryer parts, alphabet letters, saxophone mouthpieces, violin chin-rests, and a multitude of novelties such as combs, hairbrush backs and handles, pen and pencil parts, pipe stems, jewelry, handles, knives, umbrella handles, bathroom fixtures, vases, desk sets, and decorative miscellanies.

By filling in the cavities of molded letters with a lacquer of color contrasting with that used to cover the rest of the masked-off back, pleasing three-dimensional effects can be obtained in name-plate or bezel designs.

Unusually long articles can be injection molded of methacrylates by "zone molding," in which the mold cavity is maintained at progressively higher temperatures as the distance from the sprue increases.

An important specialty use of molded methacrylates has been found

in dentures. Materials used in this application are mixtures of polymer and monomer. The latter serves as a plasticizer to facilitate molding under the relatively low pressures which can be tolerated by dental molds. It is then converted into polymer by heat applied in molding. This technique makes it unnecessary to use a permanent plasticizer which would lower the softening temperature of the resin and might introduce odor or taste. Products of this kind, manufactured under such trade-marked names as "Lucitone" and "Vernonite," are now widely used by the dental profession. Recently, even molded methacrylate teeth have been produced.

Monomers and Partially Polymerized Resins

Monomeric methacrylates are utilized to impregnate such porous materials as wood, marble, tile, paper, fabrics, and anatomical specimens. Polymerization *in situ* then results in reinforcement of the treated material.

Anatomical, biological, botanical, zoological, and other specimens are preserved by imbedding them in solid blocks of methacrylate resin. This is done by immersing the specimen in partially polymerized ethyl methacrylate and completing polymerization thereof, this technique having been developed by Charles Sando of the Bureau of Chemistry and Soils in the Department of Agriculture. Rigid metallographic specimens are also often imbedded in methacrylates, but in this instance, compression molding with powder is preferred.

Adhesives for bonding various surfaces, especially for uniting cast or molded methacrylate parts, can be formulated from monomeric or partially polymerized acrylic resins by incorporation of a little peroxide catalyst therein, with or without added plasticizer or polymerized resin.

Solutions and Emulsions

Safety Glass. For several years, polymethyl acrylate sold under the trade name "Plexigum" enjoyed favor as the interlayer in "Plexite" safety glass. An ethylene dichloride solution of the resin is spread out upon clean glass sheets which are subsequently passed through a long dust-free drying oven equipped with solvent-recovery apparatus. After evaporation of the solvent, the sheets are inspected for small bubbles which, if found, are punctured by hand with a hypodermic needle filled with resin solution. The inspected sheets are then assembled with top, uncoated, glass plates and the units are bonded under heat and low pressure, preferably in a compressed-air autoclave.

This type of safety glass was first produced before the evolution of polyvinyl butyral resin, and thus it competed primarily with cellulose

acetate. It possessed a point of superiority to the latter in that no edge-sealing was required because of the absence of plasticizer and because of maintenance of the bond in humid atmospheres. The finished sheets could therefore be cut by jobbers in the manner described in a



Courtesy The Resinous Products and Chemical Co.

Figure 216. The "Acryloids," acrylic resins for coatings, are produced in this installation. The unit is unusual in that outdoor equipment such as this is common in the petroleum industry, but is quite novel in the chemical industry where sheltered equipment is customary.

preceding chapter and now used for polyvinyl butyral high-test safety glass.

Miscellaneous Solutions and Emulsions. Solutions and emulsions of various acrylics are used as adhesives for paper, textiles, cellophane, and other surfaces. They are also used for special lacquer formulations, al-

though the cost of these resins has thus far militated against their general acceptance in the customary types of surface coatings. Baking enamels for wire-coating possessing good dielectric properties, for impregnation of coils, and for abrasion-resistant coatings on rubberized cloth are special lacquer applications in which the acrylics have met with some success.

With the exception of lacquer emulsions where a solvent is present, so-called resin emulsions are, in fact, dispersions. They may be prepared either by Banbury reduction of resins in bulk or by actual emulsion polymerization of monomer. The particle size of the latter type is considerably smaller than in the case of mechanically prepared dispersions.

Both solutions and emulsions of acrylics find important uses in textile stiffening, such as the manufacture of fused collars, and in textile sizing and finishing agents to improve hand, tensile strength, and wear-resistance. They are also utilized to reduce slippage of certain textile constructions. Dispersions of resins possessing relatively high softening points are used for imparting dullness to such textiles as rayon, acetate, and nylon fabrics.

They are used in waterproof paper coatings, and in finishing genuine leather, where excellent flexibility and adhesion are obtained without sacrifice of appearance.

In these applications, various polymers and copolymers of methyl and ethyl acrylates and methacrylates, and polymers of ethyl, *n*-propyl, *n*-butyl, and isobutyl methacrylates are employed, as well as various copolymers and tripolymers of methyl acrylate, methyl methacrylate, and vinyl acetate.

Acrylic resin solutions are sold under the trade name "Acryloid." Emulsions are available under many trade names such as "Acrysol," "RHoplex," "Primal," "Methacrol," and variously numbered grades of "Onyx Resin Dispersions" prepared with either cationic or anionic surface-active agents.

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Chapter 19

Contact Resins

*Copolymers of Unsaturated Polyesters.—Doubly Unsaturated Monomers.
Allyl Resins*

General

During the past few years, intense interest has been aroused in the construction of resin-impregnated laminates by the application of little or no pressure, with or without heat. Developments of this nature were spurred on by the wartime emergency. It became vital for the aircraft industry to secure suitable plastics for the construction of plane parts larger than could practicably be molded under high pressure. Often large parts were required in non-standard shapes or in such small volume that construction of high-pressure molds, even where mechanically feasible, could not be justified on the basis of cost, materials consumed, and man-power hours required. The construction of special presses to handle large high-pressure moldings also posed a serious problem.

Development of such laminates, however, was not only a matter of circumventing the use of high pressure. The introduction of high-strength paper and glass fiber fabric as bases for laminates exhibiting exceptionally great strength-weight ratios further intensified activity in this field which very quickly grew to such a point that use of low-pressure, no-pressure molding technique yielded shaped plastics that were in direct competition with metal parts. Time, labor, and cost were saved on a strictly competitive basis. Air scoops, window frames, and ducts, for example, have been made from glass reinforced plastics instead of metal because they were cheaper and quicker to fabricate.

The result of these various interests has been the evolution of a new technology of low-pressure or no-pressure laminating of large shaped plastics possessing low density and high strength. Developments in this field are still progressing apace. Modifications of the better known thermosetting plastics have contributed their share to these spectacular innovations. Low-pressure laminating phenolics, ureas, and melamines which will cure satisfactorily within the range of 40 to 300 lbs/sq in have been mentioned at appropriate points in this text. In addition to modified resins of these standard types, however, new classes of plastics

have been evolved which offer great promise for use as so-called "contact resins" requiring the use of from 0 to 50 lbs/sq in pressure during cure. These "no-pressure" laminating resins are supplied by the manufacturers in the form of viscous, partially condensed, unsaturated fluids or less viscous monomeric liquids which polymerize under the influence of a peroxide catalyst, with or without the application of moderate heat, depending upon their chemical nature. They are 100 per cent resin formers, containing no solvent.

In the construction of a laminated article from one of these products, the basic sheet material is impregnated with the 100 per cent resin-forming liquid by using a doctor blade, or by dipping, brushing, or spreading with a roller or squeegee.

The sheet, either before or after impregnation, is wrapped around an inexpensive mold and cured by allowing it to stand at room temperature, or, more often, by application of moderate heat. Fabricators on the West Coast are using a "sunlight" catalyst. They lay up a large piece, *e.g.*, a boat, and set it out in the sun to cure. This procedure is claimed to give satisfactory results. Light pressures ranging from a fraction of a pound to about 10 lbs/sq in may be applied to intricate shapes in order to ensure intimate contact of the plastic with the mold and prevent localized segregation of free resin. Some manufacturers recommend pressures of 25 to 70 lbs/sq in in shaping formed sections. A rubber or neoprene bag, inflated with compressed air or steam, may be used as a source of the requisite pressure in the case of shaped sections. Polyvinyl alcohol sheeting is also used in bags for prototypes. Flat sheets may be cured under nothing more than the contact pressure of the covering material, such as plate glass. Inasmuch as polymerization of these unsaturated ester-type contact resins is frequently inhibited by exposure to the air, as well as by contact with sulfur, sulfur-containing compounds like vulcanized rubber, and copper, lead or mercury in some cases, glass sheets or a formed metal shape or some other impervious surface must often be used to protect the laminate during cure. Cover sheets of cellophane or polyvinyl alcohol are used to prevent exposure to the atmosphere and also to ensure formation of a smooth, glossy surface and easy removal from the mold. In some cases, as with "Plaskon" 911 laminates, successful results with metal molds can be attained by use of such lubricants as "Aquarex" D (du Pont) or "Vejin" A3 (Vejin, Inc., Cincinnati). Silicone greases are also used as mold lubricants.

No-pressure molds may be constructed from numerous inexpensive materials, such as plaster-of-Paris, concrete, wood, or cast metals. Cast phenolic resins may also be used. There is now much interest in plaster-of-Paris impregnated with various resins. With non-metallic molds, metal facing is usually necessary. Capping can be carried out by means of

formed sheet metal, by electrodeposition, or by metallizing with a spray. In any event, it increases the cost of the mold so that some of the advantage of cheapness of the principal material of construction is sacrificed. Metal lining of the mold is required in order to facilitate removal of heat created during exothermal polymerization of the resinifying liquid. If heat is not removed, low-boiling monomers are apt to be vaporized, resulting in a blistered article.

The greatest amount of interest in contact resin laminates has centered around the use of "Fiberglas" (trade mark of the Owens-Corning Fiberglas Corporation) as a base. This material possesses an exceptionally high strength-weight ratio among available textiles. Being synthetic, its fibers are also continuous and uniform in properties. It possesses excellent resistance to impact and low water absorption. It is preferable to eliminate or at least alter partially the nature of the size used in manufacturing "Fiberglas" fabrics by heating the latter to temperatures within the range of 400 to 700° F. Excellent mechanical properties are developed, for example, by heat-treating the glass cloth at about 400° F for approximately two hours before laminating. Tensile strength is not appreciably affected by this treatment, but edgewise compressive and flexural strengths may be doubled, as indicated by Table 89 for the case of "Thalid" X-500 series laminates.

Table 89. Effect of Heat-Treating "Fiberglas OC-64" on Strength Properties of "Thalid" X-500 Series Laminates *

Strength	Heat-Treated Cloth	Non-Heat-Treated Cloth
Tension	40,000-50,000	40,000-50,000
Edgewise Compression	40,000-50,000	20,000-25,000
Flexure	60,000-70,000	30,000-35,000

* Manufacturers' data. Monsanto Chemical Company.

Although heat-treating alone gives good results, the best technique to date involves removal of the starch type size from the glass either by heat-treating or by a washing operation followed by heat-cleaning. This gives a bare glass surface. By the application of proper after-treating materials ("Fiberglas" Finish 14), results comparable to heat-treating are obtained. The laminates are white and lose little or no strength upon exposure to high humidities or immersion in water.

Cooperative developments of the Owens-Corning Fiberglas Corporation and the Aircraft Laboratory, Engineering Division, U. S. Army Air Forces, Materiel Command, Wright Field, have shown that the interlaminar strength of glass fabric base laminates can be increased by incorporation of fine glass fibers in the resin prior to impregnation of the fabric. The diameter of the fibers used is about one-sixth that of the textile fibers. They are employed to the extent of about 3 per cent of

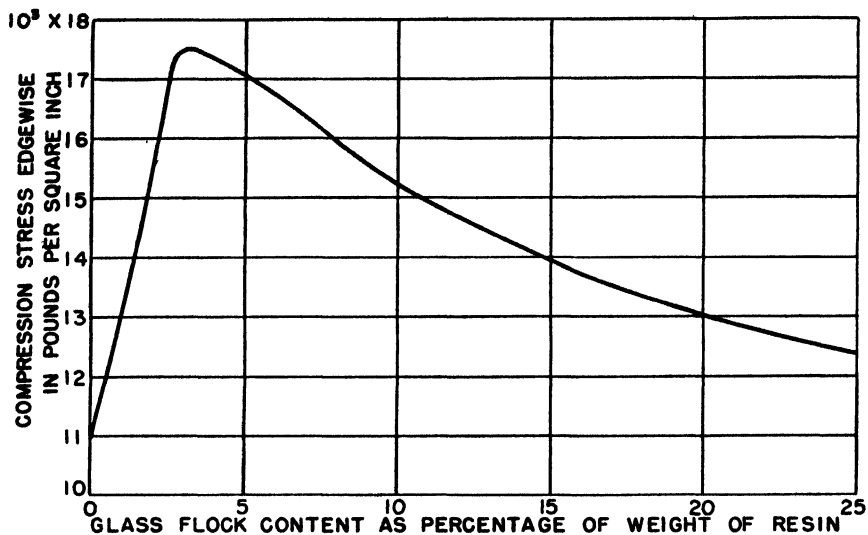


Figure 217. Relation between compressive strength and the amount of glass fiber flock introduced into a typical low-pressure laminate based on non-heat-treated glass cloth. (Kemmer⁹)

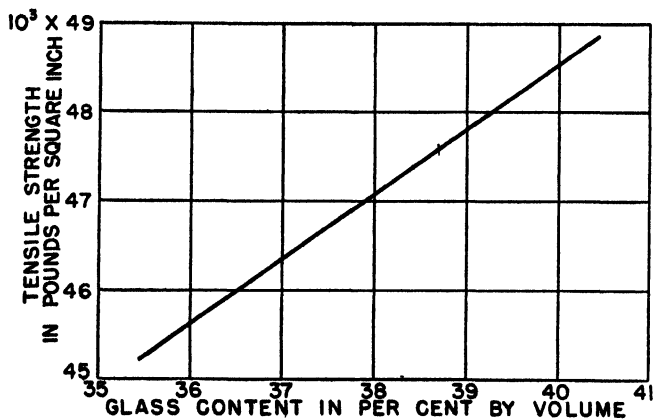


Figure 218. Relation of tensile strength to the percentage of glass fiber in typical low-pressure laminates based on glass cloth. (Kemmer⁹)

the weight of resin. The effect of these fibers upon compressive strength is shown in Figure 217.

In general, the tensile strength of no-pressure laminates based on glass fiber fabric is proportional to the glass content, as shown in Figure 218.

Directional strength effects caused by the mechanical structure of the glass fabric may be equalized to some extent by variation of the direction of lamination. Nearly equal strength in all directions can now be achieved by proper weave of the cloth or by laying fibers in the direction in which the load is required. Laying parallel fibers in a regular pattern turned through arcs of 0° , 60° , and 120° gives a strength pattern practically circular. Average properties of no-pressure laminates prepared from a number of different resins and from cross-laminated glass fiber fabric are listed in Table 90.

By the introduction of no-pressure laminating, the use of complicated and expensive equipment required for high-pressure laminating is obviated. Shaped articles can be readily formed whereas they present almost insuperable difficulties in high-pressure laminating. Comparison of the properties listed in Table 90 with those of aluminum indicates that no-pressure laminates possess advantages in higher specific strengths in tension, compression, and flexure. They are also superior in both sound and heat insulation. Fabricated surfaces may be made smoother because of the absence of rivets. Fabrication advantages may also be achieved. Against these advantages are the disadvantages of lower elongation and bearing strength.

The principal applications of no-pressure laminates to date have been in the fabrication of non-structural parts of military planes, such as fairings, cover plates of many types, doors, gasoline tanks, flaps, stabilizer tabs, etc. Production of structural parts is under development. Excellent test results have been obtained upon an experimental fuselage built of glass fiber fabric laminated with a contact resin and sandwiched with a balsawood core held in place by bonding with the same resin during the curing operation. Innovations in the automotive industry are to be expected.

Much work has been done on the development of core materials and sandwich constructions. Recent honeycomb-structure cores are illustrated in Figure 221.

Current no-pressure laminating resins consist essentially of unsaturated esters which can be polymerized either alone or in admixture with other unsaturated monomeric substances, to yield thermo-hardened, cross-linked polymers. The fundamental requisite of these esters is the presence of at least two polymerizable double bonds in their unit structure. There

Table 90. Average Properties of Contact Resin Laminates Based on "Fiberglas" ^a

Property ^a	Direction of Load	(SHEETS, NOMINAL THICKNESS, 1/4 IN.)							
		Resin A OC-64 Cloth	Resin B OC-64 Cloth	Resin C OC-64 Cloth	Resin D OC-64 Cloth	Resin E OC-64 Cloth	Resin F OC-64 Cloth	Resin G ^b OC-64 Cloth	Resin H ^b ECC-11-112 Cloth
Tension, psi	Longitudinal Transverse 45°	50,730 39,900 13,690	47,720 42,820 14,000	43,560 44,120 19,140	44,910 39,790 13,780	46,270 42,580 14,810	46,400 43,960 14,399	54,720 45,740 19,570	43,360 43,069 24,370
Compression, psi	Longitudinal Transverse 45°	43,230 31,680 16,300	40,540 40,740 17,490	48,000 41,620 20,400	40,410 46,540 21,110	51,080 47,160 17,740	46,670 44,540 16,830	54,180 56,820 27,930	36,570 39,520 23,400
Flexure, psi	Longitudinal Transverse 45°	68,150 48,100 26,500	61,900 59,090 28,350	61,150 49,700 33,850	62,560 58,300 26,150	72,500 58,660 26,860	71,189 63,790 27,900	84,600 62,600 40,920	45,350 50,700 34,880
Modulus of elasticity, psi	Longitudinal Transverse 45°	2.33 × 10 ⁶ 1.86 × 10 ⁶ 2.97 × 10 ⁶	2.24 × 10 ⁶ 2.02 × 10 ⁶ 2.64 × 10 ⁶	2.27 × 10 ⁶ 2.05 × 10 ⁶ 2.51 × 10 ⁶	2.00 × 10 ⁶ 1.83 × 10 ⁶ 2.04 × 10 ⁶	2.16 × 10 ⁶ 1.98 × 10 ⁶ 2.71 × 10 ⁶	2.10 × 10 ⁶ 2.00 × 10 ⁶ 2.67 × 10 ⁶	2.49 × 10 ⁶ 2.13 × 10 ⁶ 2.98 × 10 ⁶	2.18 × 10 ⁶ 2.19 × 10 ⁶ 2.32 × 10 ⁶
In flexure	Longitudinal Transverse 45°	2.27 × 10 ⁶ 2.27 × 10 ⁶ 1.05 × 10 ⁶	2.11 × 10 ⁶ 2.11 × 10 ⁶ 0.95 × 10 ⁶	1.89 × 10 ⁶ 1.89 × 10 ⁶ 0.79 × 10 ⁶	1.79 × 10 ⁶ 1.79 × 10 ⁶ 0.97 × 10 ⁶	2.19 × 10 ⁶ 2.19 × 10 ⁶ 1.13 × 10 ⁶	1.82 × 10 ⁶ 1.82 × 10 ⁶ 0.78 × 10 ⁶	2.34 × 10 ⁶ 2.34 × 10 ⁶ 1.36 × 10 ⁶	2.45 × 10 ⁶ 2.45 × 10 ⁶ 0.26 × 10 ⁶
Proportional limit, psi	Longitudinal Transverse 45°	24,500 15,400 5,730	23,800 11,360 6,900	31,000 18,400 6,000	23,800 24,500 4,660	15,710 15,760 18,750	28,609 15,909 9,609	82,250 21,100 15,100	10,500 8.5 × 10 ⁻⁴ 7.3 × 10 ⁻⁴
Coeff. thermal exp., cm/cm °F	Longitudinal Transverse —	6.9 × 10 ⁻⁴ — —	5.1 × 10 ⁻⁴ 7.4 × 10 ⁻⁴ —	8.6 × 10 ⁻⁴ 9.7 × 10 ⁻⁴ —	6.6 × 10 ⁻⁴ 9.0 × 10 ⁻⁴ —	7.7 × 10 ⁻⁴ 9.7 × 10 ⁻⁴ —	7.8 × 10 ⁻⁴ 8.5 × 10 ⁻⁴ —	8.2 × 10 ⁻⁴ 8.9 × 10 ⁻⁴ —	8.5 × 10 ⁻⁴ 7.3 × 10 ⁻⁴ —
Water absorption, %	—	0.6 —	0.3 —	0.4 —	0.6 —	0.3 —	0.5 —	0.4 —	—
Chemical resistance, %	—	110 —	111 —	110 —	115 —	115 —	112 —	117 —	119 —
Aviation gasoline, weight increase	—	—	0.0 —	—	—	0.0 —	—	1.23 —	—
"Freosone," weight increase	—	—	0.6 —	0.0 —	0.1 —	0.1 —	—	0.77 —	—
Flammability, burning rate, in per min	—	Self-extin- guishing	0.247 —	0.271 —	Self-extin- guishing	0.251 —	Self-extin- guishing	0.4 —	Self-extin- guishing
Glass content, %	—	—	—	—	—	—	—	—	—
By weight	—	60.8 —	53.1 —	52.3 —	49.2 —	54.2 —	54.7 —	53.4 —	54.7 —
By volume	—	38.2 —	39.5 —	39.7 —	35.9 —	37.9 —	40.8 —	39.2 —	41.2 —
Specific gravity	—	1.71 —	1.73 —	1.81 —	1.73 —	1.69 —	1.77 —	1.76 —	1.78 —

^a The above properties have been determined by means of procedure outlined in L-P-406 Federal Standard Stock Catalog, Section IV, Part 5, "Federal Specification for Elastics, Organic; General Specifications (Method of Tests)."

^b Flaked fibers omitted.

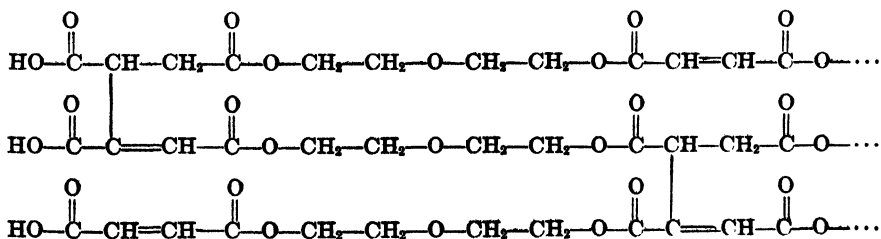
are two general categories of such esters available at present. The first type comprises unsaturated linear polyesters produced from a glycol and maleic acid, or some other unsaturated dicarboxylic acid as, for example, "Carbic" anhydride. Such polyesters may obviously be modified with unsaturated alcohols like allyl alcohol. The presence of double bonds in the polyester chain permits subsequent copolymerization with other added monomeric unsaturates such as styrene. Because of the polymeric character of the ester, these resins are moderately viscous before polymerization, a fact which has been found to facilitate mechanical handling during impregnation by use of a doctor blade or by roller coating.

The second type of no-pressure laminating resin consists of doubly unsaturated monomeric esters. Important commercial representatives of this group include monomolecular esters of allyl alcohol and dibasic acids or their derivatives which still contain two esterifiable carboxyl groups. Although allyl resins have recently become of importance, other unsaturated alcohols can be used also.

Obvious modifications of this second group include monomeric esters of unsaturated alcohols and unsaturated mono- or dibasic acids, such as allyl itaconate and glycol or polyglycol esters of unsaturated acids, such as methacrylic acid. These monomeric liquids are non-viscous, because of their low molecular weight, and must be used with care in laminating operations in order to avoid resin segregation in shaped sections.

Copolymers of Unsaturated Linear Polyesters

It has been shown in Chapter 11 that a linear polyester is produced as the result of esterification of a glycol with a dibasic acid. Where an aliphatic acid is used, the polymer is often balsam-like. If unsaturated glycols, such as butene-diols, or unsaturated dicarboxylic acids like maleic, fumaric, or itaconic acid are employed, the resulting polyester possesses double bonds which are capable of polymerizing, under catalytic influence, to yield cross-linked, tridimensional resins. A portion of the structure of a polymer derived from diethylene glycol maleate, for example, can be represented as follows:



On 24 hours' standing at room temperature, diethylene glycol maleate containing about 2 per cent of added benzoyl peroxide is converted from a viscous liquid to an insoluble, hard, rubbery gel. On heating this gel at 50° for 48 hours, it is transformed into a hard, tough, transparent, and easily machined cast plastic having a Rockwell L hardness of about 55. The same result is attained by heating the unsaturated polyester with catalyst at 50° for 50 hours without preliminary standing at room

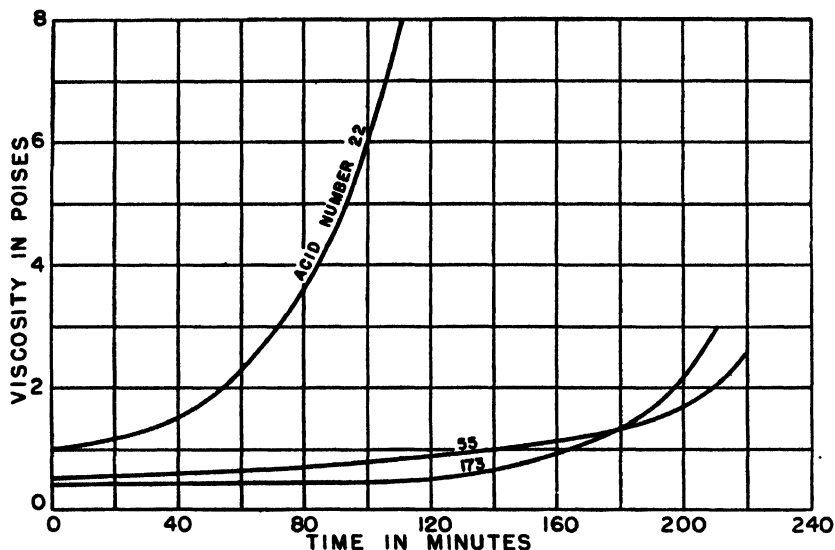


Figure 219. Increase in viscosity of 1:3 mixtures of vinyl acetate and polymeric maleic esters of diethylene glycol of various degrees of condensation (as indicated by acid number) where copolymerized at 90° under reflux. Viscosity measured on Gardner-Holdt scale at 25°.

<i>Acid No. of Polyester</i>	<i>Average Number of Maleic Condensation Units</i>
173	1.65
55	5.40
22	13.61

(Kropa and Bradley¹⁰)

temperature. Such prolonged curing times are impractical for commercial products. It has been found that polymerization can be greatly speeded, and cast plastics of valuable properties obtained, by copolymerizing these unsaturated polyesters with such resin-forming monomeric compounds as vinyl acetate, styrene, or methyl methacrylate. Cross-linked, tridimensional resins are thus formed similar to those illustrated in the preceding formula, but in which one or more units of the copolymerizing material bridge some, at least, of the alkyd chains at the points directly united in the formula given above.

Numerous factors influence the formation of such copolymers, the more important being (1) degree of condensation, *i.e.*, molecular weight of the polyester; (2) components of the polyester; (3) nature of the copolymerizing monomeric unsaturate; (4) ratio of polyester to monomeric unsaturate; (5) type and amount of catalyst; (6) temperature; and (7) mass of the polymerizing mixture.

Figure 219 shows the effect of degree of condensation of polydiethylene glycol maleate upon the rate of increase of viscosity where copolymerized with vinyl acetate at 90°.

Under properly controlled conditions, clear transparent copolymers are obtainable. The ratio of reactants exercises a marked effect upon transparency, however, for if the concentration of vinyl monomer is sufficiently high, it will polymerize by itself at the same time that it copolymerizes with the unsaturated polyester. The two polymers are, in some instances, incompatible with each other; hence where the concentration of vinyl monomer is sufficiently high to yield straight vinyl polymers, cloudy or opaque polymeric mixtures may result. In the case of polyesters of diethylene glycol and maleic acid, up to about 32 per cent of vinyl acetate or styrene yields transparent products; polyesters combined with 1/1 vinyl acetate—styrene mixtures will give clear copolymers up to 40 per cent of monomer content, while methyl methacrylate yields transparent resins in all proportions.

Benzoyl peroxide, lauroyl peroxide, and acetyl benzoyl peroxide are among the most effective catalysts for bringing about these copolymerizations. The influence of catalyst content upon rate of copolymerization is shown in Table 91.

Table 91. Influence of Catalyst Content on Rate of Resinification at 50° of Vinyl Acetate-Diethylene Glycol Maleate Solutions^{18, a}

Benzoyl peroxide, %	0.005	0.01	0.02	0.03	0.05	0.1
Resinification rate, hours:						
Partial gel	—	—	—	—	—	—
Complete gel	20	—	—	—	—	—
Hard gel	45	20	20	20	—	—
Soft resin	100	80	80	60	20	—
Hard resin	160	140	140	130	90	24

^a 68 per cent polyester of acid no. 55.5.

The influence of temperature upon copolymerization of vinyl acetate and polydiethylene glycol maleate is shown in Table 92.

Resins of this category are especially useful in cast form, with or without fillers. They are light in color and can be made water white by careful control of the quality of reactants. They are almost completely light stable. They can be produced in Rockwell L hardnesses ranging from 50

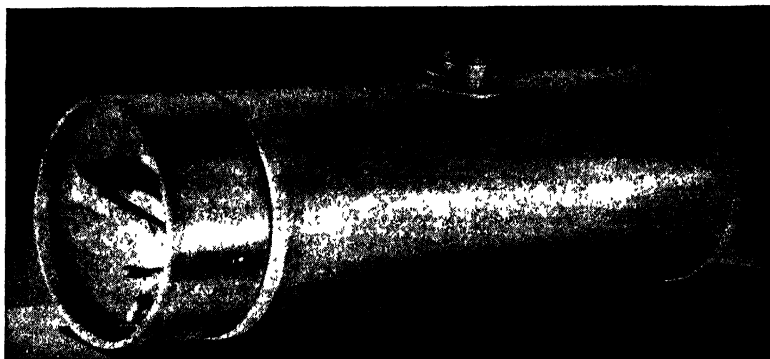
Table 92. Influence of Temperature on Rate of Resinification at 50° of Vinyl Acetate-Diethylene Glycol Maleate Solutions^{18, a}
(Catalyst: 0.0033% benzoyl peroxide)

	Resinification Rate, Hours		
	39°	50°	64°
Partial gel	100	—	—
Complete gel	150	—	—
Hard gel	240	20	—
Soft resin	—	70	20
Hard resin	—	140	80

^a 68 per cent polyester of acid no. 98.1.

to 110. In general, they are considerably harder than transparent thermoplastics such as cellulose acetate or polymethyl methacrylate.

Copolymerizable mixtures of unsaturated linear polyesters and other monomeric unsaturates can be employed as described on page 498 for the impregnation of sheet materials, such as cotton or glass fiber fabric, and laminated products can then be built up and cured under little or no pressure. Limited attempts have been made to produce commercial



Courtesy American Cyanamid Co.

Figure 220. Canvas-filled "Laminac" water tank.

resins of this general type under the name "Elfolite." "Laminac" belongs to this category. Other commercial products of comparable character have been developed, such for example as "Bakelite" BRS-16631 and BRS-17582, recently replaced by "Bakelite" BRS-69 and BRS-78, respectively.

"Laminac" contains no solvent. It cures, out of presence of air, with lauroyl or benzoyl peroxide (0.3 to 1.0 per cent) in 30 minutes at 100–110° with little or no pressure. It shrinks 10 to 11 per cent during polymerization. Table 93 lists properties of unfilled cast polymer and of typical laminates based on canvas and glass fiber fabric.

Table 93. Properties of "Laminac" *

<i>Physical Properties</i>	Unfilled Cast Polymer	Glass Fiber Fabric Laminate ^{a, b}	Canvas Laminate ^{b, c}
Specific gravity (25°)	1.23	1.70	—
Index of refraction (n_D^{25})	1.535	—	—
Micro hardness (Bierbaum)	26.3–39.1	—	—
Rockwell hardness			
M scale	91–94	84	—
R scale	118–120	97	—
Ultimate tensile strength, psi			
at – 40°	7270	47,300–43,100	6370–6600
25°	6270	41,300–33,100	4990–6090
after 24 hr water immersion, tested wet			
80°	3850	23,100–26,700 ^c	3790–4230
Elongation immediately before fracture,			
25°, %	—	3.4–4.9	3.6
Modulus of elasticity in tension, psi (25°)		1.34–1.11 × 10 ⁶	0.22 × 10 ⁶
After 24 hr water immersion			0.33 × 10 ⁶
Load, psi			
0 (extrapolated)	0.35 × 10 ⁶	—	—
70	0.35 × 10 ⁶	—	—
2820	0.29 × 10 ⁶	—	—
4220	0.21 × 10 ⁶	—	—
Flexural strength, Dynstat, kg/cm ² (25°)	893	1710–1620	—
Flexural strength, psi			
at – 40°	15,300	—	—
25°	13,900	—	—
80°	6,380	—	—
Modulus of elasticity in flexure, psi			
at – 40°	0.44 × 10 ⁶	1.67–1.47 × 10 ⁶	—
25°	0.31 × 10 ⁶	1.66–1.45 × 10 ⁶	—
80°	0.15 × 10 ⁶	1.35–0.94 × 10 ⁶	—
Compressive strength at 25°, psi	26,400 ^d	50,900 (flatwise)	—
Impact strength, Izod notched, per in notch	0.19	—	—
Impact strength, Dynstat (25°), kg/cm ²	12.9	—	—
Shrinkage during cure, %	10–11	—	—
Distortion under heat, °C—A.S.T.M.	100	—	—
Burning rate, in/min, 0.073 in sample	1.1	0.88–0.67 (0.066 in sample)	—
<i>Electrical properties</i>			
Power factor, A.S.T.M.			
at 60 cycles	0.011	—	—
at 10 ⁶ cycles	0.031	0.02	—
at 25 × 10 ⁶ cycles	—	0.04	—
Dielectric strength, A.S.T.M. short time			
test, ½ in, v/mil	520	—	—
Dielectric constant, A.S.T.M.			
at 60 cycles	4.2	—	—
at 10 ⁶ cycles	3.5	5	—
at 25 × 10 ⁶ cycles	—	6	—
Loss factor, A.S.T.M.			
at 60 cycles	0.053	—	—
at 10 ⁶ cycles	0.120	—	—
Arc resistance, A.S.T.M.	90–126	—	—
(Material burns on failure)			
Volume resistivity, ohms	—	10 ¹²	—

Table 93. Properties of "Laminac" * (Continued)

<i>Chemical properties</i>	Unfilled Cast Polymer	Glass Fiber abric Laminate ^{a, b}	Canvas Laminate ^{b, c}
Gain in weight during 24 hours' immersion at 25°, %			
Distilled water	0.46	1.3	1.87
Aromatic gasoline	0.23	1.0	—
Benzene	0.76	3.0	—
Acetone	2.58	6.9	—
Gain in weight during 15 min immersion in boiling water, %	—	0.5	—

* "Fiberglas" ECC-162. 4-ply; 45% resin. 0.5% "Alperox" C as catalyst; curing temperature: 100° (45 min). 30 psi. Thickness: 0.065 in. Weight, lb/sq ft: 0.597.

^b First value given is perpendicular to warp; second parallel to warp.

^c 14-oz canvas; 2-ply; 60% resin. 0.5% "Alperox" C as catalyst; curing temperature: 100° (30 min). Contact pressure. Thickness: 0.078 in.

^d Material flows during test.

* By using the treatment described on page 499, this wet strength figure would be 80 to 100 per cent of the dry strength.

* Manufacturers' data. American Cyanamid Company.

Properties of various "Fiberglas" laminates prepared by use of two different grades of "Laminac" are given in Tables 94 to 96.

Table 94. Properties of "Laminac" 4125—"Fiberglas" Laminates. Parallel Laminated. All Tests Run in Parallel Direction*

Resin	4125	4125
Resin Content, %	40	40
Filler	ECC-162HT	ECC-162HT
No. Plies	8	4
Pressure, psi	Separators	50
Cure	30 min—105°	30 min—105°
Density, gms/cc	1.74	
24 hr Absorption, %		
Water		1.7
Gasoline		0.4
2B Alcohol		0.7
Flexural Strength, psi		
25°	31,200	
80°	23,200	
Modulus in Bending, psi × 10 ⁶		
25°	2.30	
80°	1.75	
Power Factor at 10 ⁶ c/s		0.025
Dielectric Constant at 10 ⁶ c/s		4.4
Power Factor at 3 × 10 ⁹ c/s		0.017 †
Dielectric Constant at 3 × 10 ⁹ c/s		4.42 †
Barcol Hardness		70

* Manufacturers' data. American Cyanamid Company.

† Run on 7 ply ECC-128HT Laminate. 35% Resin.

Table 95. Properties of "Laminac" 4125—"Fiberglas" Laminates. Parallel Laminated. All Tests Run in Parallel Direction. Tested According to A.S.T.M. Specifications*

Resin	4125	
Resin Content, %	40-45	
Filler	ECC-162HT	
Pressure, psi	50	
Cure	30 min-105°	
Bonding Strength, lbs	1,120	
Compressive Strength, psi Edgewise	14,900	
Tensile Strength, psi	41,500	
Tensile Modulus, psi $\times 10^6$	2.25	
Flexural Strength, Flatwise psi	} Samples ½" Thick	27,900
Flexural Strength, Edgewise psi		29,400
Deflection at Break, Flatwise mils		> 100
Deflection at Break, Edgewise mils		> 100
Izod Impact, Flatwise, Ft lbs/in Notch		33
Heat Distortion, °C		354
Flammability, in/min		0.9
Dimensional Stability, mils/in		0.26
Coefficient of Thermal Expansion $\times 10^6$ per °C, Av.		9.0
Power Factor at 60 c/s		0.013
Dielectric Constant at 60 c/s		5.2
Arc Resistance, Sec, Av		81
Dielectric Strength, v/m		230

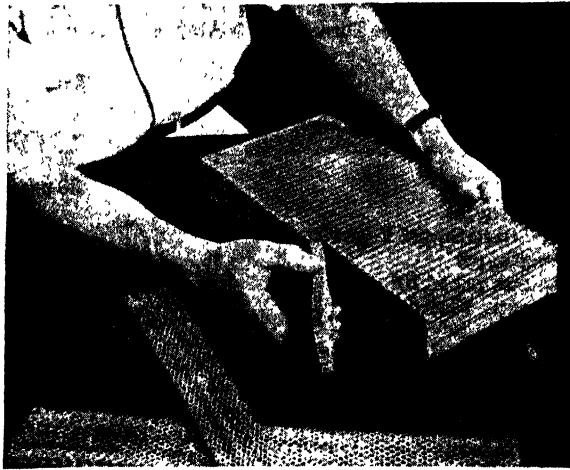
* Manufacturers' data. American Cyanamid Company.

Table 96. Properties of "Laminac" 4201—"Fiberglas" Laminates *
(Parallel Laminated. All Tests Run in Parallel Direction)

Resin	4201	4201
Resin Content, %	40	40
Filler	ECC-162HT	ECC-162HT
No. Plies	8	4
Pressure, psi	Separators	70
Cure	30 min—105°	30 min—105°
Density, g/cc	1.76	
24 hr Absorption, % Water		1.8
Gasoline		0.3
2B Alcohol		0.6
Flexural Strength, psi 25°	34,100	
80°	21,000	
Modulus in Bending, psi $\times 10^6$, 25°	2.30	
80°	1.65	
Power Factor at 10 ⁶ c/s		0.022
Dielectric Constant at 10 ⁶ c/s		4.7
Power Factor at 3×10^6 c/s		0.019 †
Dielectric Constant at 3×10^6 c/s		4.50 †
Barcol Hardness		62

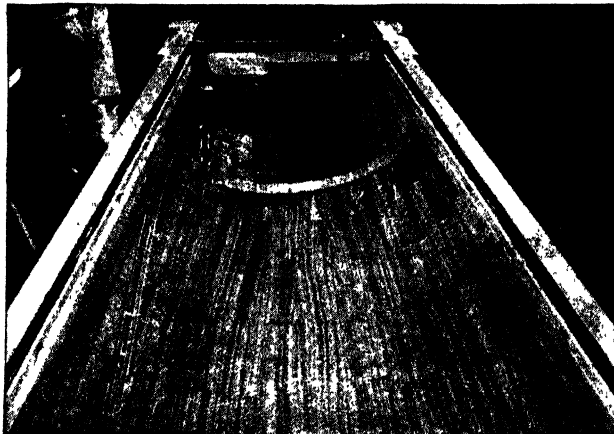
* Manufacturers' data. American Cyanamid Company.

† Run on 7-ply ECC-128HT laminates 35% resin.



Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 221a. An important new development in low-pressure laminating consists of a sandwich of parallel laminates of "Plaskon" 911 resin and glass cloth, separated by and bonded to a feather-weight honeycomb core made of the same resin reinforced by glass cloth. (above) Honeycomb core having a cross-section comprising $3/16$ inch diameter hexagons.



Courtesy Plaskon Division, L.-O.-F. Glass Co.

Figure 221b. Half-mold of fuselage section with outer skin, half of resin bulkhead preform, honeycomb core, and tubular higher density core in place.

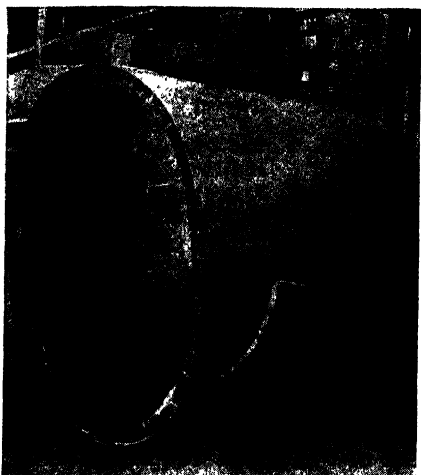


Figure 221c. Completed fuselage section with two half portions welded into single unit by final molding operation.

Courtesy Plaskon Division, L.-O.-F. Glass Co.

Other low-pressure, no-pressure resins which appear to be of the polyester type are available under such designations as "Plaskon" 900 and 911, "Thalid" X-500 series (Monsanto), "Selectron" 5000 series (Pittsburgh Plate Glass), certain "Marco" ("MR") resins (Marco Chemicals), some of the "Vibrins" (Naugatuck), and "Paraplex" P-10 (Resinous Products).

"Plaskon" 900 is supplied in two component parts which are admixed by the fabricator just before using, after first dissolving 2 per cent of benzoyl peroxide catalyst in one of the liquids. "Plaskon" 911-11 resin is supplied as a liquid to which 4 per cent of a readily soluble paste catalyst is added before using. At room temperature, 900 possesses a viscosity of about 8,000 cps.; 911-11, about 65,000. Care must be exercised in polymerizing thick sections because the reaction is highly exothermic and excessive temperatures may be attained by lack of adequate control. Suggested curing times for laminates up to 1/32 inch in thickness are given in Table 97.

Table 97. Curing Conditions for "Plaskon" 911-11 *

Temperature of Curing Medium (°C)	Time Required for Cure
70	9 hours
80	3 hours
90	1 hour
100	30 minutes
110	15 minutes
120	8 minutes
150	1-2 minutes

* Manufacturers' data. Plaskon Division, L.-O.-F. Glass Co.

The range of physical properties obtainable with "Plaskon" 911-11 laminates is shown in Table 98.

Table 98. Physical Properties of "Plaskon" 911-11 Resin Laminates *

Physical Property	Materials Being Laminated			
	Heat-Treated "Fiberglas" Cloth	Cotton Cloth	Paper	
	Normal Value	Maximum Value	Normal Value	Normal Value
Water absorption in 24 hr	0.2 to .5%	—	1 to 3%	1 to 3%
Compressive strength	40,000 to 60,000 psi	70,000 psi	16,000 to 30,000 psi	16,000 to 30,000 psi
Tensile strength	40,000 to 70,000 psi	—	20,000 psi	—
Flexural strength	55,000 to 75,000 psi	100,000 psi	20,000 psi	20,000 to 25,000 psi
Young's modulus in flexure (stiffness)	2,500,000 to 3,000,000 psi	3,500,000 psi	400,000 to 700,000 psi	700,000 to 1,000,000 psi
Density	1.75 to 1.85	—	1.4	1.4

* Manufacturers' data. Plaskon Division, L.-O.-F. Glass Co.

"Thalid" X-500 series resins are supplied as slightly viscous fluids which are admixed with about 12 per cent of their own weight of monomeric styrene and 0.5 per cent benzoyl peroxide prior to casting or laminating. Physical properties determined in accordance with Federal Specifications LP-406 on laminates consisting of 1/4 inch panels of heat-treated, cross-laminated OC-64 "Fiberglas," with a resin content of 45 per cent by weight (59 per cent by volume) are given in Table 99.

Table 99. Characteristics of Typical Glass Fabric Laminates Based on "Thalid" X-500 Series Resins *

Property	Unit	Direction of Load	Value
Tension	Psi	Longitudinal	46,000
	Psi	Transverse	44,000
	Psi	45°	14,000
Compression	Psi	Longitudinal	46,500
	Psi	Transverse	44,500
	Psi	45°	16,500
Flexure	Psi	Longitudinal	71,000
	Psi	Transverse	63,500
	Psi	45°	27,500
Modulus of Elasticity in Tension	Psi	Longitudinal	2.1×10^6
	Psi	Transverse	2.0×10^6
Modulus of Elasticity in Flexure	Psi	Longitudinal	2.6×10^6
	Psi	Transverse	1.8×10^6
	Psi	45°	0.75×10^6
Proportional Limit in Flexure	Psi	Longitudinal	28,500
	Psi	Transverse	15,500
	Psi	45°	9,500
Coefficient of Thermal Expansion	cm/cm/° F	Longitudinal	7.8×10^{-6}
	cm/cm/° F	Transverse	8.5×10^{-6}
Water Absorption	%		0.5
Hardness, Rockwell	M		112
Chemical Resistance			
Aviation Gasoline	% loss		0.2
"Prestone"	% loss		0.1
Flammability, Burning rate	in per min		Self-extinguishing
Specific Gravity			1.77

* Manufacturers' data. Monsanto Chemical Company.

The "Selectrons" are quick-curing resins supplied as monomeric liquids which are polymerized by heating at temperatures up to 250° F after addition of a suitable catalyst such as benzoyl peroxide or tertiary butyl hydroperoxide. Properties of "Selectron" 5003 monomer are listed in Table 100.

Table 100. Properties of Typical "Selectron" 5003 Monomer*

Color	Pale yellow
Specific Gravity at 77° F	1.13
Viscosity at 77° F. cps.	470-550
Flash Point, ° F	75
Shrinkage during cure, %	7-8
Stability of liquid in dark at 77° F	Greater than 5 months
Stability of liquid in dark at 150° F	10 days
Tank Life of liquid at 80° F:	
in presence of 0.8% of benzoyl peroxide	20 hr
in presence of 0.8% of tertiary butyl hydroperoxide	2 hr

* Manufacturers' data. The Pittsburgh Plate Glass Company.

Properties of unfilled cast "Selectron" 5003 and of laminates based on this resin are given in Tables 101 and 102.

Table 101. Properties of Unfilled Cast Polymer, "Selectron" 5003 *

Physical Properties

Specific Gravity at 77° F	1.220
Hardness: Barcol Impressor	52
Rockwell, M scale	115
Tensile Strength, psi at 80° F	4,000
Flexural Strength, psi at 80° F	5,800
Compressive Strength, psi at 80° F	21,300
Modulus of Elasticity in Flexure, psi	550,000
Modulus of Elasticity in Compression, psi	490,000
Tan. Prop. Limit in Compression, psi	15,700
Unnotched Izod Impact Strength, ft lb	0.70
Abrasion Resistance, Taber (Plexiglas)	1
Abrasion Resistance to Falling Emery (Plexiglas)	2.5
Heat Distortion Point, ° C	90

Chemical Resistance

Water Absorption:	
% after 24 hr at 77° F	0.46
% after 4 hr at 212° F	0.99
Acetone Absorption, % (A.S.T.M.)	Disintegrates
Benzene Absorption, % (A.S.T.M.)	0.39
Chloroform Absorption, % (A.S.T.M.)	Disintegrates
Aviation Gasoline Absorption, % (A.S.T.M.)	0.05

Heat Stability

Degree of Checking	0
Time of Checking, hours	Greater than 48
Weight Loss, % after 1 hr at 240° F	0.36

* Manufacturers' data. The Pittsburgh Plate Glass Company.

Table 102. Properties of Typical Laminates Based on "Selectron" 5003 *

<i>Laminate Data</i>			
Base Material	<i>Cotton Muslin</i>	<i>"Fiberglas" QC-64</i>	<i>Heat-Treated ECC-128</i>
Fiber Orientation	Parallel	Crossed	Cross Woven
Catalyst	0.8% Bz ₂ O ₂	0.8% Bz ₂ O ₂	0.8% Bz ₂ O ₂
Cure	2 hr at 170° F 1 hr at 250° F	2 hr at 170° F 1 hr at 250° F	2 hr at 170° F 1 hr at 250° F
Pressure	Contact	Contact	Contact
Thickness, in	1/8 & 1/2	1/8 & 1/2	1/8 & 1/2
Resin Content, %	66 & 61	45 & 42	45 & 38
<i>Physical Properties</i>			
Specific Gravity at 77° F	1.307	1.594	1.650
Hardness: Barcol	41	58	64
Rockwell M	101	114	114
Tensile Strength, psi	8,400	36,300	35,000
Flexural Strength, psi	11,200	64,300	37,900
Compressive Strength, psi	15,000	37,400	23,000
Mod. Elast. Tension, psi	1,040,000	2,110,000	2,480,000
Mod. Elast. Flexure, psi	1,050,000	2,280,000	2,370,000
Mod. Elast. Compression, psi	590,000	1,940,000	1,950,000
Tan. Prop. Limit in Compr., psi	4,000	37,000	21,900
Notched Izod Impact Strength, ft lb	0.54	20.2	14.6
Bonding Strength (corr. value 1/2 in), psi	1,238	1,520	1,389
Burning Rate, in/min	0.48	0.48	0.47
<i>Chemical Resistance</i>			
Water Absorption, % (A.S.T.M.)	0.74	0.35	0.45
% (4 hr at 212° F)	2.10	0.96	0.81
Acetone Absorp., % (A.S.T.M.)	7.67	6.40	5.53
Benzene, % (A.S.T.M.)	0.18	0.10	0.06
Chloroform, % (A.S.T.M.)	25.51	32.36	21.63
Aviation gasoline, % (A.S.T.M.)	0.08	0.35	0.23
Acetone Insoluble, % (A.S.T.M.)	99.2	98.2	98.4

* Manufacturers' data. The Pittsburgh Plate Glass Company.

While "Selectron" 5003 is a hard, rigid plastic, 5009 possesses a degree of flexibility approaching that of polymethyl acrylate. Inasmuch as these resins are compatible in all proportions, physical properties between these two limits of rigidity and flexibility can be obtained.

Characteristic properties of "Vibrin" 103 are given in Table 103. "Vibrin" 120 yields a flexible resin on curing.

According to the manufacturer, free "Vibrin" surfaces should be covered with impervious sheets to insure proper cure and eliminate surface softness. This requirement is characteristic, to a greater or less degree, of all contact resins currently available, although suppliers of a few of them lay claim to freedom therefrom. In this connection it is pertinent to recall the theory of Barnes concerning inhibition of polymerization of methacrylates by the presence of excess oxygen. (See pages 462-463 for discussion of this subject.)

Table 103. Properties of "Vibrin-103" Resin *

Specific gravity	1.28
Vol. shrinkage on curing	9.4 %
Unnotched Izod impact strength at room temperature	10.3 ft lb/in ²
Flexural strength at room temp.	17,000 psi
Young's modulus at room temp.	240,000 psi
Rockwell hardness at room temp.	M-80
Elongation at break	5 to 10% (est.)
Refractive index	1.533
Electrical Properties	
Volume resistivity	6×10^{13} ohm-cms
Dielectric constant (50 cycles)	5.1
Loss factor (50 cycles)	0.17
Dielectric strength (.005" sample)	2,000 v/mil
Chemical Resistance (A.S.T.M. 1 week immersion at room temp.)	
Distilled water	1.05% absorption
30% Sulfuric Acid	0.45% absorption
3% Sulfuric Acid	0.87% absorption
10% Nitric Acid	0.95% absorption
10% Sodium Hydroxide	† 2.11% absorption
1% Sodium Hydroxide	0.87% absorption
95% Ethyl Alcohol	† 2.03% absorption
Acetone	† 9.5% absorption
Carbon Tetrachloride	0.20% absorption
Gasoline	Nil

* Manufacturers' data. Naugatuck Chemical.

† Eventually cracks.

Certain "MR" resins, manufactured by Marco Chemicals, Inc., and available in laminated form under the designation "Marcolite" (Continental Can Company) are analogous contact resins. "MR-17" is a current grade. Average properties of various types of "Marcolite" are listed in Table 104.

Resins of the low-pressure, no-pressure type have also been developed for use as impregnants and sealants of porous metals, such as aluminum and magnesium castings. Among materials evolved for this purpose are "Thalid" X-100 series resins and "Ault and Wiborg No. 988 Metal Impregnating Compound." These products are low molecular weight polyesters which are admixed with styrene and thermo-hardened after impregnation of the metal casting by vacuum technique.

Contact Resins Produced from Doubly Unsaturated Monomers

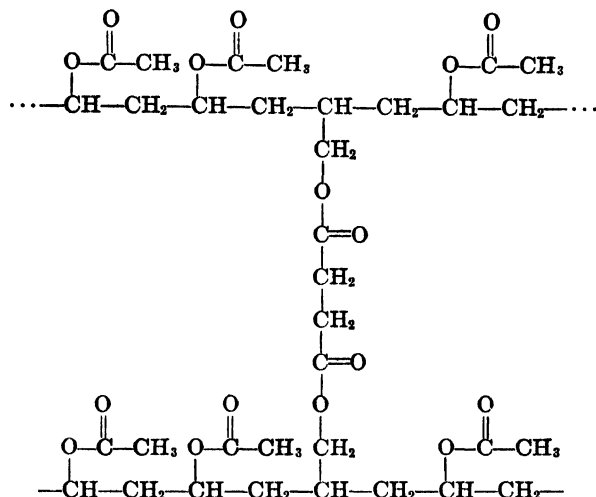
Allyl Resins. Despite the fact that allyl acrylate was polymerized to a hard, insoluble, and infusible mass as early as 1873, it was commonly supposed for years that compounds possessing the allyl configuration were incapable of polymerization. In 1939, however, B. S. Garvey, Jr., working in laboratories of the B. F. Goodrich Company, reported that copolymerization of a small amount of diallyl succinate with vinyl

Table 104. Average Properties of Various Types of "Marcolite" *

	"FIBERGLAS"				COTTON 4-oz. Muslin Crossed	PAPER Kraft Crossed
	Parallel	OC-63	Crossed	ECC-11-162 Crossed	ECC-11-127 Crossed	
Moisture absorption, %	0.3		0.3	0.3	0.5-1.2	3.0-5.0
Gasoline absorption, %	0.0		0.0	0.0	0.0	0.0
Specific gravity	1.97		1.65-1.85	1.66-1.80	1.40-1.48	1.4
Burning rate (in/min)	Self-extin- guishing		0.33	0.36	0.44	0.35
Tensile strength (psi)	102,000	40,000-55,000		30,000-40,000	8,500-12,000	13,000
Modulus in tension (psi)	5,960,000	1,500,000-2,800,000		1,750,000	1,000,000	1,000,000
Flexural strength (psi)	65,000	40,000-50,000		30,000-40,000	20,000	19,000
Compression strength, flatwise (psi)	41,000	60,000-70,000		60,000-70,000	32,000	34,000
Compression strength, edgewise (psi)	26,000	25,000		20,000	20,000	16,000
Impact, Notched Izod, ft lb/in notch	130	40-60		30-50	2.9-3.4	0.9-1.0
Impact, Notched Izod, ft lb/sq in	500	200-300		200-250	18-20	5.5-6.4
Hardness, Rockwell M	100	100		110	92	93
Shear (psi)	33,600	21,000		18,000	12,000	11,000
Bearing (psi)	16,000	30,000		27,000	20,000	20,000
Thermal expansion $\times 10^{-5}/^{\circ}\text{C}$		2.8		1.3-2.2	1.0-2.6	
Heat distortion, $^{\circ}\text{C}$		170		160		
Dimensional stability, %		L, W, T = 0.0, 0		L, W, T = 0.0, 0		
% Elongation in 2" gage		2.2		2.9	2.5	2.2

* Manufacturers' data. Marco Chemicals, Inc.

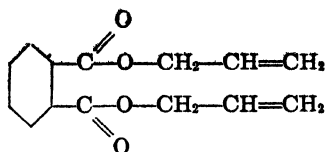
acetate, using benzoyl peroxide as a catalyst, resulted in a cross-linked or "vulcanized" polymer lacking thermoplasticity. A characteristic segment of its structure may be represented as follows:



Where the amount of diallyl succinate is between 0.01 and 0.1 per cent, solubility of the polymer is somewhat less than that of polyvinyl acetate itself, but thermoplasticity is not greatly affected. More than one per cent of diallyl succinate yields products which are neither soluble nor thermoplastic.

The use of diallyl succinate as a "vulcanizable plasticizer" for previously prepared polyvinyl acetate was also developed by Garvey. The resin is first plasticized with this monomeric ester and the latter is then polymerized with the aid of heat and a catalyst to yield a product which shows much lower plasticity and solubility than the original polyvinyl acetate. Garvey explains this change in the initial resin as being caused by the development of mechanical cross-linking of the linear chains of the acetate by the complex three-dimensional structure of the allyl polymer intimately entangled therewith. So-called "vulcanizable plasticizers" like diallyl succinate have been found useful in decreasing thermoplasticity of a wide range of materials, including not only polyvinyl acetate, but also the corresponding chloride, polystyrene, polymethyl methacrylate, cellulose acetate, shellac, asphalt, ester gum, and halogenated naphthalenes and biphenyls.

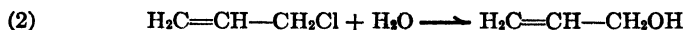
Shortly after these developments by Goodrich became known, it was announced that the Shell Development Company was undertaking the production and exploitation of resins made by polymerization of diallyl phthalate,



This company had just introduced a commercial process for making allyl alcohol from propylene by high temperature chlorination of this olefin:



followed by hydrolysis:



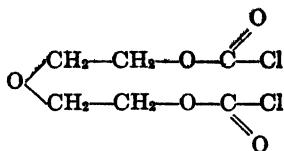
Allyl alcohol is now also produced from propylene by the Carbide and Carbon Chemicals Corporation through other intermediates.

Initial interest in Shell's diallyl phthalate polymers was reported to lie in the field of tin can liners.

Shell is now offering a diallyl phthalate laminating varnish in the form of a 50 per cent solution of partial polymer in toluene. Volume shrinkage of the polymer during final cure is about four per cent. *Tert*-butyl perbenzoate, with or without added benzoyl peroxide is recommended as a catalyst. By use of proper pre-curing technique, this diallyl phthalate varnish resin can be adapted to use of laminating pressures ranging from 150 to 4000 psi.

Because of the presence of two polymerizable double bonds in this ester, resinous polymers of diallyl phthalate are tridimensional.

In 1941 the Pittsburgh Plate Glass Company announced a series of allyl resins of undisclosed nature, known first as "Columbia Resins" and recently re-named "Allymers." While a whole family of numbered "Allymers" has been described, "CR-39" has been especially stressed. This material, possessing two allyl groups in its monomeric unit, is capable of polymerizing to a tridimensional plastic. It is produced as a fluid, water-white monomer. According to the 1943 Americana Annual, "CR-39" is diallyl ethylene glycol dicarbonate. It seems more likely, however, that "CR-38" corresponds to this derivative of ethylene glycol, while "CR-39" is probably the corresponding compound derived from diethylene glycol and, in turn, is obtained from an intermediate recently offered for sale by the Pittsburgh Plate Glass Company; namely, diglycol chloroformate²⁴:



Upon addition of a peroxide catalyst, the "Allymers" can be cast into transparent sheets (known as "Allites") and other shapes approaching the methacrylates in clarity. Curing is carried out at temperatures of 70 to 115°. During polymerization, the liquid first becomes a viscous fluid and then a gel before it hardens. Shrinkage during polymerization is about 14 per cent.

Although "CR-39" possesses excellent clarity in sheet form, there is a slight yellowish edge color and some slight tendency toward discoloration (yellowing) upon weathering.

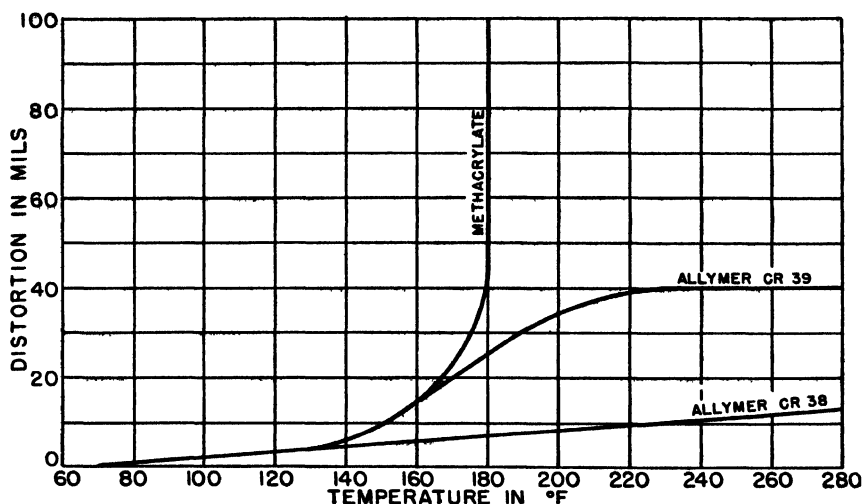


Figure 222. Comparison of heat resistance of certain transparent plastics as measured by ASTM heat distortion test D-48-47. (Adapted from Pechukas, *Strain, and Dial*¹⁴)

"Allite CR-39" possesses greater abrasion resistance than transparent thermoplastics like the methacrylates. Although cross-linked, it undergoes limited deformation with heat at about the same temperature as the methacrylates and can be formed by similar methods at 95–105°, although it is somewhat more restricted in formability. It cannot, for example, be deep-drawn. While this material is comparable to polymethyl methacrylate insofar as initial temperature of deformation under load is concerned, it differs from the latter markedly in that increase of temperature beyond a certain maximum does not cause further deformation. This anomalous behavior is illustrated in Figure 222.

It is reported that clear sheets of "Allite CR-39" do not craze under stress, even upon exposure to solvent vapors. In this respect "CR-39" is reported to be superior to polymethyl methacrylate and polystyrene. The

burning rate of "CR-39" is only about one-third that of polymethyl methacrylate. Unlike monomeric methyl methacrylate, the monomer of "CR-39" can be stored indefinitely without change, even without addition of an inhibitor.

"Allymer CR-39" can be used for manufacture of no-pressure laminates. In curing sheets up to one-eighth inch in thickness, enclosed between glass plates and heated in air, the manufacturer recommends heating for 2 hours at 80°, followed by 2 hours at 100°, or a rising temperature cycle in which the oven temperature is gradually raised from 82 to 115° over a period of 4 hours.

In order to decrease curing time or reduce flow in the early stages of polymerization, so as to prevent resin segregation, it is sometimes desirable to polymerize "Allymer CR-39" partially, until a thick syrup is formed, before carrying out impregnation. After thickening, cooling retards further cure so that the viscous fluid may be kept for several hours, or even days, at room temperature.

Typical physical properties of cast transparent "CR-39" and of laminates are given in Tables 105 and 106.

Table 105. Properties of Clear Cast "Columbia" Resins²²

	C.R. 39-1	C.R. 39Bd	C.R. 149
Specific gravity (25/4°)	1.31	1.38	1.34
Refractive index (20°): n_D	1.50398	1.51	1.52
n_C	1.50131	—	—
n_F	1.51002	—	—
Dispersion factor, $\frac{n_D - 1}{n_F - n_C}$	57.84	—	—
Hardness			
Knoop	11 to 14	16 to 19	19 to 22
Barcol Impressor, 15 sec	26 to 30	38 to 42	48 to 54
Rockwell, M scale	95 to 100	110	117
Cold flow, Barcol Impressor, 15 sec	8 to 11	4 to 5	4 to 6
Plastic yield, in (1000 lb, 1/2-in cube):			
Room temperature	0.006	0.002	0.003
Room temperature plus 50°	0.022	—	—
Abrasion resistance:			
Mar resistance:			
Taber, times that of methacrylate	30 to 40	20 to 30	18 to 25
Falling emery,			
times that of methacrylate	8 to 10	5 to 8	3 to 5
times that of glass	1.2 to 1.4	0.7 to 1.0	0.7 to 1.0
Wear resistance, times that of methacrylate	2 to 3	—	—
Tensile strength, 25°, psi	5,000 to 6,000	7,000 to 9,000	11,000 to 13,000
Modulus of rupture, psi:			
50° (122° F)	5,000 to 6,000	11,000 to 14,000	—
25° (77° F)	8,000 to 10,000	20,000 to 25,000	26,000
- 10° (14° F)	13,000 to 15,000	—	—
- 57° (- 70° F)	14,300	—	—

Table 105 — (Continued)

	C.R. 39-1	C.R. 39Bd	C.R. 149
Modulus of elasticity in flexure, psi:			
50° (122° F)	160,000 to 200,000	200,000 to 250,000	—
25° (77° F)	250,000 to 330,000	440,000 to 470,000	550,000
— 10° (14° F)	370,000 to 400,000	—	—
— 57° (— 70° F)	340,000	—	—
Compressive strength:			
Ultimate, psi	22,800	25,000 to 27,000	26,000
Modulus, psi	230,000	300,000 to 400,000	400,000
Impact strength, 25°, ft lb per in:			
Izod, notched	0.3 to 0.4	0.3 to 0.4	0.3 to 0.6
Charpy, notched	0.3 to 0.4	—	—
Izod, unnotched	2 to 3	4 to 6	3 to 4
Charpy, unnotched	3 to 4	5 to 8	—
Specific heat, cal per g per ° C	0.55	—	—
Thermal expansion, linear coefficient per ° C			
— 40° to — 10°	0.00007	—	—
— 10° to + 25°	0.000087	—	—
25° to 50°	0.000107	—	—
95° to 120°	0.000153	—	—
Thermal conductivity:			
Cal per cm per sec per sq cm per ° C	0.0005	—	—
Btu per in per sq ft per hr per ° F	1.45	—	—
Heat distortion:			
Temperature producing 10 mils distortion, ° C	55 to 70	95 to 105	65 to 70
Distortion at 130°, mils	35 to 65	25 to 35	175 to 190
Maximum recommended operating temperature under no load ^a :			
Continuous service	100° (212° F)	135° (275° F)	100° (212° F)
Intermittent (1-hr duration)	150° (302° F)	—	150° (302° F)
Burning rate, 1/8-in sheet, Navy test, in per min	0.3	0.5	0.4
Warpage	0.00	—	—
Light transmission before aging, white, per cent	90 to 92	—	—
Haze before aging	1 to 2	—	—
Light transmission after aging, white, per cent	89 to 91	—	—
Water absorption, per cent	0.2 to 0.4	0.2	0.2
Power factor:			
1 kc	0.012	—	—
1 mc	0.057	—	—
Dielectric constant:			
1 kc	3.8	—	—
1 mc	3.6	—	—
Dielectric loss:			
1 kc	0.047	—	—
1 mc	0.20	—	—
Dielectric strength (samples 1/16 inch thick):			
Short-time, v per mil	570	—	—
Step-by-step, v per mil	525	—	—
Resistance to chemical reagents—gain in wt. after 7 days immersion, per cent:			
Distilled water	0.7	0.7	0.5 to 0.7
30% H ₂ SO ₄	0.5	—	—

Table 105 — (Continued)

	C.R. 39-1	C.R. 39Bd	C.R. 149
3% H ₂ SO ₄	0.7	—	—
10% HNO ₃	0.7	—	—
10% HCl	0.4	—	—
10% NH ₄ OH	0.8	—	—
10% NaOH	0.5	—	—
1% NaOH	0.6	—	—
2% Na ₂ CO ₃	0.6	—	—
1% NaCl	0.6	—	—
3% H ₂ O ₂	0.7	—	—
95% ethyl alcohol	0.1	—	—
50% ethyl alcohol	0.5	—	—
Acetone	0.5	0.4 to 0.6	0.2
Ethyl acetate	0.3	—	—
Carbon tetrachloride	0.6	—	—
Chloroform	1.5	0.6	—
5% acetic acid	0.6	—	—
Gasoline	0.1	0.1	—
Oleic acid	0.2	—	—
Benzene	0.7	—	—
Toluene	0.6	—	—

* Under special conditions, such as use of a "CR-39-1" sheet as the inner panel of a heated-air de-icing window, "CR-39-1" has performed satisfactorily over long periods with 240° F air on one surface and room temperature air on the opposite surface.

Table 106. Physical Properties of "C.R. 39" Laminates ²²

	Kraft Paper		Hurlbut 716 Paper (Pulp Paper)		Mitscherlich Paper (Spruce Sulfite)	
Density, 25°	1.38		1.40		1.41	
Resin, per cent	58		58		45	
Hardness:						
Barcol	36		40		39	
Rockwell, M scale	98		94		—	
Cold flow, Barcol	7		6		6	
Water absorption, 24 hr at 25°, per cent	3.9		2.4		8.5	
	Machine Direction	Cross Direction	Machine Direction	Cross Direction	Machine Direction	Cross Direction
Tensile strength, psi	21,600	10,700	12,200	11,200	25,600	10,400
Modulus of rupture, psi	22,600	17,400	18,400	16,800	25,800	16,400
Modulus of elasticity, psi	1,190,000	780,000	940,000	800,000	2,090,000	820,000
Compressive strength (edgewise), psi	14,500	13,600	—	—	14,100	12,900
Impact strength (notched Izod), ft-lb per in	0.91	0.6	1.0	1.0	1.1	0.90
	8-oz. Duck		360 Cotton Sheeting		Exeter Print Cloth	
Density, 25°	1.37		1.38		1.38	
Resin, per cent	61		58		65	
Hardness:						
Barcol	22		32		36	
Rockwell, M scale	72		87		91	
Cold flow, Barcol	7		7		7	
Water absorption, 24 hr at 25°, per cent	1.5		1.1		0.9	

Table 106 — (Continued)

	Warp	Fill	Warp	Fill	Warp	Fill
Tensile strength, psi	9,000	7,200	12,000	6,200	16,500	7,300
Modulus of rupture, psi	14,100	13,100	17,400	11,600	20,000	11,200
Modulus of elasticity, psi	420,000	360,000	570,000	470,000	760,000	480,000
Compressive strength (edgewise), psi	13,700	13,200	—	—	17,700	16,300
Impact strength (notched Izod), ft-lb per in	3.7	3.6	1.7	1.4	1.8	1.0

	C.R. 39Bd ^a Heat-treated OC-64 "Fiberglas"	C.R. 39Bd Standard OC-64 "Fiberglas" Plies Crossed	C.R. 39Bd Heat-treated OC-64 "Fiberglas" Plies Crossed	C.R. 149 Heat-treated OC-64 "Fiberglas" Plies Crossed
Density, 25°	1.77	1.89	1.85	1.75
Resin, per cent	41 to 44	39	40	40
Hardness:				
Barcol	57	45	60	70
Rockwell, M scale	108	107	113	117
Cold flow, Barcol	6	7	5	3
Water absorption, 24 hr at 25°, per cent	0.4	1.9	1.4	0.3
Acetone absorption, 1 week at 25°, per cent	0.7	1.7	0.7	0.2

	Warp	Fill			
Tensile strength, psi	85,000 to 100,000	4,600	54,100	53,400	53,400
Modulus of elasticity, psi	4,160,000	1,010,000	2,600,000	3,100,000	2,840,000
Modulus of rupture, psi	113,500	6,600	55,500	72,200	87,800
Modulus of elasticity, psi	3,320,000	1,130,000	2,650,000	2,150,000	2,640,000
Compressive strength, psi:					
Edgewise	60,700	20,600	28,000	42,500	54,400
Tangent proportional limit	59,600	12,250	26,500	38,300	52,900
Modulus of elasticity	3,320,000	—	2,310,000	2,160,000	2,360,000
Shear strength, psi	29,200	5,400	—	22,500	26,500
Fatigue limit, 10,000,000 cycles, psi	—	—	—	22,500	—
Bonding strength, psi	1,980	—	1,260	1,800	1,849
Impact strength (notched Izod), ft-lb per in	over 25.3	1.1	30	27	over 26

^a Fabric plies oriented with all warp threads parallel

Figures 223 and 224 compare the mar resistance of transparent sheets of glass, "Allite CR-39," and cast polymethyl methacrylate.

"MR-1A" ("Marco" Resin 1A) is an allied allyl resin which has found especial utility in combination with "Fiberglas." The tensile strength of cast, unfilled "MR-1A" is in the order of 6200 lb/sq in. Its modulus in tension averages 370,000 lb/sq in. Its density is 1.2. Stress-strain curves of various "Fiberglas" laminates constructed with "MR-1A" are given in Figure 225.

Table 107. Physical Test Results—"MR-1A"—"Fiberglas" Laminates^a

Laminate Designation Filler, "Fiberglas" No. Number of Laminæ Stack Arrangement Nominal Thickness, in Specific Gravity	223	224	309	236	221	241
	OC-63	OC-63	OC-63	ECC-11-127	ECC-11-148	ECC-11-161
	12	12	8	18	10	8
Parallel	Crossed 90°	Crossed 90°	Crossed 90°	Crossed 90°	Parallel	Crossed 90°
Nominal Thickness, in	.104	.107	.107	.128	.124	.121
Specific Gravity	1.96	1.93	1.69	1.81	1.80	1.79
Tension						
Direction of Load	with warp				with fill	
Ultimate Load, lb	6,390	3,140	2,095	2,840	2,070	2,210
Specimen Width, in	.604	.502	.502	.502	.482	.505
Ult. Load per inch of width per lamina	880	520	520	315	430	550
Tangent Proportional Limit, psi	50,000	32,000	21,000	26,000	13,000	13,500
0.01% Offset Proportional Limit	58,000	41,000	25,000	27,500	15,000	15,500
2% Offset Yield Stress	—	58,000	—	38,700	30,800	24,300
Ultimate Tensile Stress	105,000	58,500	39,000	44,200	34,600	36,200
Young's Modulus of Elasticity, psi	5,960,000	2,800,000	1,900,000	2,100,000	1,500,000	1,900,000
Elongation at Failure (% over 2-inch length)	1.8	2.3	2.1	2.6	2.6	2.9
Compression (Edgewise)						
Direction of Load	with warp				with fill	
Ultimate Load, lb	1,340	1,380	1,580	1,393	1,000	1,200
Specimen Width, in	.496	.500	.495	.500	.500	.500
Ult. Load per inch of width per lamina	225	230	400	155	200	300
Tangent proportional limit, psi	26,100	25,950	21,500	14,000	11,000	10,000
0.01% Offset proportional limit	—	—	23,700	15,000	14,000	12,000
Ultimate compressive stress	26,100	26,000	29,000	22,500	16,900	19,600
Young's Modulus of elasticity, psi	5,500,000	3,000,000	—	2,800,000	2,200,000	2,300,000
Deformation (% over 2-inch length)	.47	.86	1.38	.86	.75	.93
Manner of Failure	diagonal shear	diagonal shear	diagonal shear	diagonal shear	diagonal shear	diagonal shear
Bending (Flatwise)						
Length, width, thickness, inches	5×1.02×.102	5×.745×.106	5×.749×.109	5×.751×.128	5×.751×.126	5×.746×.116
Span, in	3	3	3	3	3	3
Ultimate Load at center of span, lb	138	90	128	105	94	78
Tangent proportional limit, psi	55,000	41,000	45,000	17,000	19,000	19,000
Modulus of rupture, psi	59,300	48,200	64,800	38,400	35,500	34,900
Modulus of elasticity, psi	5,950,000	3,000,000	2,100,000	2,300,000	1,630,000	2,080,000
Bearing						
Hole diameter	—	.124	.124	.124	.124	.124
Nominal bearing strength (4% hole deformation)	—	28,000	23,500	20,000	29,500	23,300
Ultimate bearing strength, psi	—	32,100	31,300	38,500	34,800	34,600

Physical tests corresponding to the curves of Figure 225 are given in Table 107.

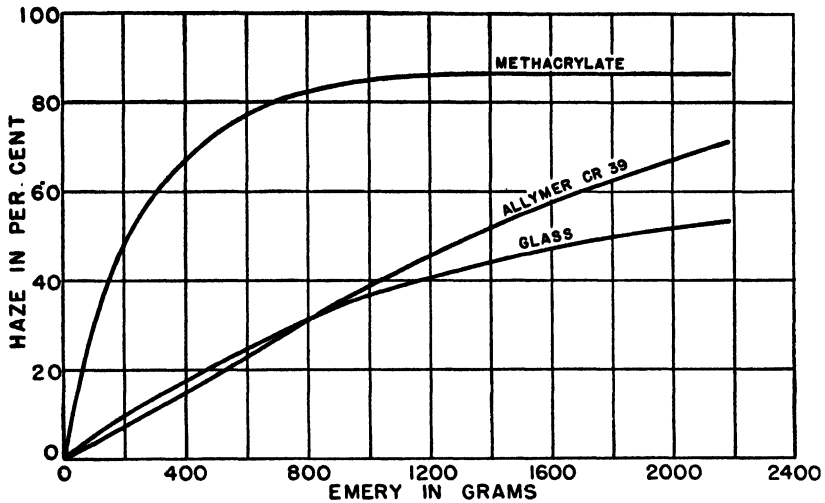


Figure 223. Comparative falling emery mar resistance (modified ASTM procedure) of "Allymer" CR 39, polymethyl methacrylate, and glass. (*Strain*²²)

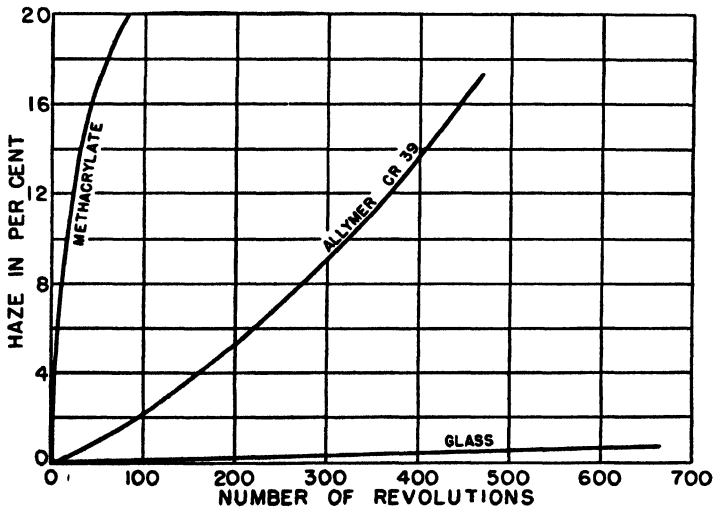


Figure 224. Comparative Taber mar resistance (CS-10 wheel) of "Allymer" CR 39, polymethyl methacrylate, and glass. (*Strain*²²)

Other properties of "MR-1A"-Fiberglas laminates are given in Table 108.

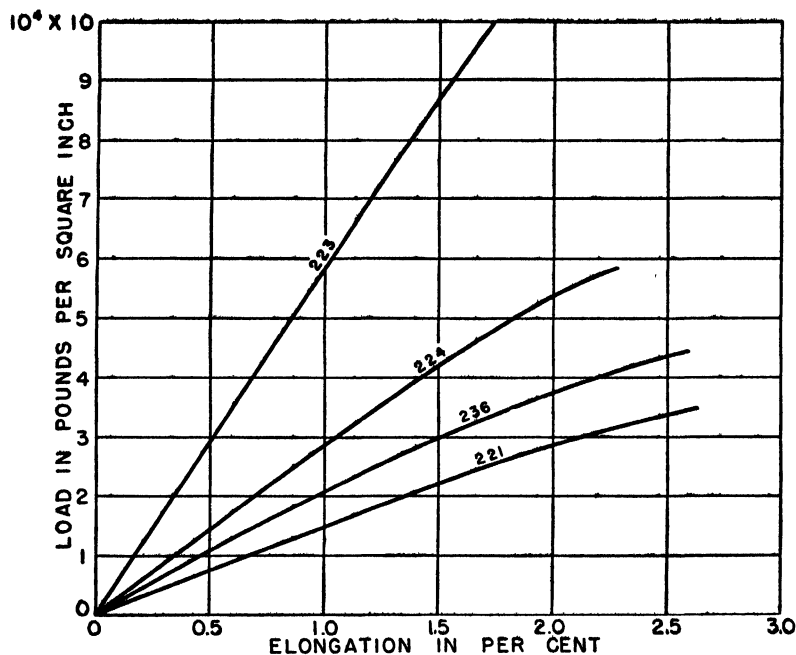


Figure 225. Stress-strain curves for various "Fiberglas" laminates bonded with MR-1A resin. Ultimate tensile stress values are given in Table 107. (Armstrong⁶)

Specific strength values of "MR-1A" laminates are compared with those of aluminum in Table 109.

The B. F. Goodrich Chemical Company has recently developed another allyl resin called "Kriston," properties of which have been given by S. L. Brous, *Modern Plastics*, 23, No. 4, 107 (Dec. 1945). A characteristic of particular interest is its low shrinkage on polymerization—3.25 to 4 per cent from monomer to polymer at room temperature.

Table 108. Average Properties of "MR-1A"—"Fiberglas" Laminates^a

Impact strength, notched Izod (ft-lb/in of notch)	25-100
Ultimate shear strength (lb/sq in)	14,000-33,000
Ultimate compressive strength, flatwise (lb/sq in)	41,000-75,000
Moisture absorption (%)	0.2-0.4
Gasoline absorption (%)	0.01-0.15
Hardness, Rockwell	71-107
Hardness, Barcol Impressor	40-65
Heat distortion (° F)	300-350
Coefficient of linear expansion (per ° F)	$2.7-5.2 \times 10^{-6}$
Burning rate (in/min)	0-0.4

Table 109. Specific Strength Values "MR-1A"- "Fiberglas" Laminates^a

Material	(1) Specific Tensile Strength (psi)	(2) Specific Tensile Modulus (psi)	(3) Specific Buckling Stability (psi)	(4) Specific Modulus of Rupture (psi)	(5) Specific Ulti- mate Bearing Strength (psi)
"MR-1A"- "Fiberglas"-223	53,500	3,040,000	790,000	15,400	—
"MR-1A"- "Fiberglas"-224	30,300	1,450,000	416,000	12,900	16,600
"MR-1A"- "Fiberglas"-309	23,000	1,120,000	435,000	22,600	18,500
"MR-1A"- "Fiberglas"-236	24,400	1,160,000	388,000	11,700	21,300
"MR-1A"- "Fiberglas"-221	19,200	833,000	280,000	10,900	19,300
"MR-1A"- "Fiberglas"-241	20,200	1,060,000	362,000	10,900	19,300
24S-T "Alclad" Aluminium Alloy	20,200	3,800,000	495,000	7,300	29,600
24S-RT "Alclad" Aluminium Alloy	22,400	3,800,000	495,000	8,100	32,400

⁽¹⁾ Specific Tensile Strength = Ult. tensile strength divided by specific gravity.⁽²⁾ Specific Tensile Modulus = Tension modulus divided by specific gravity.⁽³⁾ Specific Buckling Stability = Flexural modulus divided by (specific gravity)³.⁽⁴⁾ Specific Modulus of Rupture = Modulus of rupture divided by (specific gravity)³.⁽⁵⁾ Specific Ult. Bearing Strength = Ult. bearing strength divided by specific gravity.

Resins Produced from Other Doubly Unsaturated Monomers. It will be apparent from the preceding discussion that other doubly unsaturated monomeric esters should be capable of giving rise to contact resins. Glycol and polyglycol esters of acrylic and methacrylic acid, for instance, fall within this category. Likewise, esters of unsaturated alcohols and unsaturated acids are also subject to the generalizations heretofore drawn. Resins from such esters as allyl itaconate have been patented, while numerous Russian publications, for example, have shown interest in such esters as methallyl methacrylate.

The field of low-pressure, no-pressure resins is an important one which is rapidly expanding. Significant new developments in resins, fabricating technique, and applications in the aircraft, automotive, and other fields can be expected during the next few years.

Prices of these resins at the present time run between 60 cents and two dollars per pound.

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Chapter 20

Natural and Synthetic Elastomers

GENERAL

The rubber and plastics industries have followed separate paths during most of their history, yet these two fields of technology have much in common. The synthetic rubber program has emphasized this fact, but even before its advent the larger rubber companies had begun to give commercial expression to a growing appreciation of this relationship.

Natural rubber is a linear thermoplastic high polymer composed of exceptionally long molecules. The extreme length of these molecules permits them to exist in randomly kinked forms which, upon being stretched, tend to straighten out. Thus, under tension, rubber molecules untangle themselves and become more nearly linear. As a consequence they also become longer and align themselves more or less parallel to each other. At those points where the highest degree of orientation prevails, minute crystallites are developed. An individual molecule may traverse several of these microcrystalline regions. This crystalline character is more pronounced in rubber which is stretched rapidly than in that which is extended slowly. The tensile strength of rubber increases upon stretching, in much the same manner as orientation augments the strength of pseudo-crystalline plastics like nylon and saran. Unlike these plastics, however, the uncoiling and parallel orientation of rubber molecules is only transitory. The latter return to their original randomly kinked configuration as soon as stress is relieved. It is this characteristic which causes rubber to exhibit the phenomenon of reversible extensibility, commonly called elasticity.

At temperatures which are sufficiently low to make molecular motion sluggish, stretched rubber remains in the oriented, microcrystalline state and is said to be "racked." It is interesting to note that the molecular alignment of racked rubber is reflected in the fibrous character of fractured particles.

Although innumerable articles and many volumes have dealt with the science and technology of rubber, and although x-ray studies, in particular, have contributed enormously to our understanding of this

material, much of its chemistry still remains an enigma. It is fortunate, however, that remarkable advances in rubber technology have not had to await physical and chemical elucidation of its nature.

As with natural rubber, the phenomenon of reversible extensibility in synthetic rubbers can also be traced to the uncoiling of kinked molecular chains of great length. The extent to which synthetic elastomers exhibit crystallization upon stretching, however, as shown by x-ray diffraction patterns, varies according to chemical species. Where some cross-linking occurs during their formation, or where the polymeric structure is unsymmetrical, crystallization is at a minimum or does not appear at all.

Unlike reversible extensibility, the attribute of vulcanizability is not related to the agglomerate molecular character of an elastomer, nor is it a necessary corollary of elasticity. Many plasticized linear polymers—so-called “elastoplastics”—like vinyl chloride-acetate copolymers and ethyl cellulose, exhibit elastomeric character, but are not vulcanizable. Even apart from these substances, a number of macromolecular materials like polyisobutylene require no plasticizer for the development of elasticity although they cannot be vulcanized in the ordinary sense. The ability of an elastomer to undergo vulcanization depends upon the presence of reactive points, somewhere in its molecular structure, making it possible to establish cross-linkages between several linear chains. Such intermolecular bridges may be the result of direct union between reactive groups brought about with the aid of heat or a metallic oxide, for example, as in the vulcanization of neoprene and “Thiokol.” More often, however, cross-links are introduced by reaction of the elastomer with an added chemical like sulfur, as in the case of rubber and the “Bunas.” The thermal sensitivity of the elastomer is reduced by the development of tridimensionality upon vulcanization. Plasticity is decreased. Tensile strength is improved. Solubility in various liquids which dissolve the uncured elastomer is considerably decreased. Other physical properties may also be affected. These results are reminiscent of the change in character of polystyrene brought about by copolymerization with a trace of divinyl benzene. We have already seen examples of vulcanization in preceding chapters. The cross-linking of polyvinyl alcohol with dibasic acids, of polyethylene maleate with vinyl acetate, of “Petrex” polybasic acids with ethylene glycol, of methyl acrylate polymers by treatment with quinone dioxime, and of “Norepol” by reaction with sulfur are reactions of this category. The vulcanization of rubber and various synthetic rubbers is an analogous phenomenon.

The extent of cross-linking during vulcanization may be a function of the number of reactive groups in the elastomer, the degree of completeness with which they can enter into reaction with added chemicals, the

amount of vulcanizing agent employed, the presence and nature of the curing agents, accelerators, and activators, and the conditions of cure. In natural rubber and in most butadiene polymers and copolymers the amount of unsaturation is large and all of the double bonds are reactive. Cross-linking by vulcanization with sulfur may therefore be very great, provided enough sulfur is added. Where only a small amount is employed, the netting index is low and the restriction of the chains is at a minimum so that extensibility is not impaired, while recovery from stretching, that is decrease of permanent set, is materially improved. The products possess the well-known and valuable properties of soft rubber. The plasticity of the raw elastomer is decreased while elasticity and strength are less sensitive to temperature. Where sufficient sulfur is introduced to react with most of the unsaturation present, a high netting index results and the product is hard, like ebonite. In the case of certain elastomers like neoprene and "Thiokol" which are normally vulcanized in the presence of metallic oxides, the active groups do not appear capable of entering into complete reaction, for reasons yet unknown. Vulcanization develops only low netting indices and therefore only products resembling soft rubber can be obtained from these particular elastomers.

In the case of "Butyl" rubber, the degree of reactive unsaturation is purposefully limited to a very small amount. Only slight cross-linking can therefore be established and the vulcanized products resemble soft rubber.

In completely saturated elastomers possessing no reactive groups, such as the polybutenes, the opportunity for vulcanization is non-existent and such materials behave like normal thermoplastics.

Nowhere in high polymer chemistry is the effect of added compounding ingredients more striking than in rubber technology. Not only are the properties of the vulcanized products contingent upon the nature and amount of curing agent used, but vulcanization itself may be greatly facilitated and controlled by the addition of accelerators and other activators of uncertain role. Antioxidants exert a pronounced effect upon the aging characteristics of soft vulcanizates which still contain unsaturation. Reinforcing fillers of a number of kinds exhibit the most sensitive influence upon the physical properties of the cured compounds. The latter effect is especially pronounced in the case of carbon black which enormously enhances the tensile strength and improves abrasion resistance of natural rubber; it is even more essential to the proper compounding of butadiene rubbers. Several other kinds of compounding ingredients are also used by the rubber industry. The total number of these additive materials is very great.

Improvement in rubber compounding technique has been clearly re-

flected in increased longevity of automobile tires. Before the general introduction of carbon black in the early 'twenties, zinc oxide filled tires could not be relied upon for more than 3000 miles of halting service! It is a far cry from 3000 to 30,000 miles, yet the latter is now commonplace, thanks to modern methods of compounding. Even during the decade of the 'thirties, mileage per tire was doubled.

The technology of natural and synthetic rubbers has reached enormous proportions. In 1940 the United States consumed 608,000 long tons of natural material. In 1945, American production of synthetic rubbers reached 700,000 tons!

This text makes no pretense of adequately covering, in a single chapter, an industry so vast. Only the general nature of the different kinds of elastomeric materials will be discussed. Specialized articles and reference works should be consulted for details.

NATURAL RUBBER

Rubber and other similar hydrocarbons occur widely distributed in nature in the latex of a very large number of plants. Among them all, *Hevea Brasiliensis* is the most important. It is the original wild rubber tree of the Amazon which was transported to the Far East where it has been cultivated on over nine million acres of plantations. About 97 per cent of the world's supply of natural rubber is grown in the Malay Archipelago and other territories of Southeastern Asia, notably Ceylon. Less successful cultivation has been attempted in Liberia and Brazil. All of these areas lie within a belt 1500 miles wide about 10° north and south of the equator, in territory having an annual rainfall of at least two meters.

A much less important industrial source of rubber is guayule, a shrub native to Mexico, now cultivated to a limited extent in borderline states of this country. The Russian dandelion, kok-sagyz, has lately been exploited with some success by the Soviets.

In 1939, total world production of crude rubber was 1,002,768 long tons, of which 486,372 tons were imported into this country. A year later, world production was 1,390,469 long tons, with American imports accounting for 58.8 per cent of the total at an average New York price of 20.1 cents per pound.

Latex

Rubber latex is a slightly acidic, milky white emulsion which usually shows a pH of about 6. Its composition varies with source, age of tree, season, and other conditions of tapping. Total solids ordinarily run between 30 and 45 per cent. Rubber and other non-rubber hydrocarbons

account for about 90 per cent of the solids, the remainder being various inorganic salts, proteins, sugars, quebrachitol, and acetone-soluble "resins," including certain fatty acids of non-resinous character. According to Kemp, the values given in Table 110 represent a typical fresh lot of normal ammonia-preserved latex.

Table 110. Typical Composition of *Hevea* Latex⁵³

Substance	Content in Per Cent Based on	
	Latex	Dry Solids
Total solids	40.02	100.00
Water and ammonia	59.98	—
Acetone extractables	2.05	5.12
Water-soluble substances	3.04	7.59
Ash	0.42	1.05
Nitrogen	0.24	0.61
Rubber hydrocarbon	33.98	84.90
Non-rubber hydrocarbon substances	6.04	15.10

The impure rubber hydrocarbon is usually separated from latex by coagulation with acetic or formic acid. Wild rubber from Brazil—so-called "Para"—is precipitated by evaporation in the heat of a smoky flame. A grade formerly available under the designation L. S. rubber was produced by spray-drying (the letters standing for "latex sprayed"). This method of coagulation has been largely abandoned and, inasmuch as wild rubber accounts for less than 3 per cent of total production, acid precipitation is most important.

After coagulation, the rubber is rolled, washed, and smoked or creped. Smoked sheet is tougher than creped rubber because it is washed by passage between rolls rotating toward each other at the same speed. Creping, on the other hand, involves tearing between rolls running at unequal speeds, so that some mastication occurs during washing.

Most natural rubber is coagulated on the plantation before shipment to this country, for it is costly to pay ocean freight on the water content of the latex. Moreover, natural latex is unstable and the rubber settles out on standing or during transit. Precipitation is partly the result of destruction of the resinous or proteinaceous protective colloids by bacterial action and oxidation.

During the past few years, methods have been developed for preserving latex and for utilizing it advantageously in many different ways, so that prior to Pearl Harbor, there was an annual upward trend in the volume shipped as such to this country. In 1939, the amount consumed in the United States corresponded to a little over 43,000 long tons of dry rubber.

Addition of alkalis, especially ammonia, to latex prevents bacterial action and stabilizes the suspension so that it can be preserved in-

definitely. Latices poor in rubber hydrocarbon usually require more ammonia than richer ones.

Two general methods for manufacture of solid rubber goods from latex have been developed. The rubber may be precipitated upon suitable forms which are first dipped in an aqueous solution of a colloid-precipitating electrolyte, such as zinc chloride, and then in latex. Occasionally, an electrically conducting form may be made the anode of a cell in which latex is used as electrolyte. Generally a porous form is used and an electrolyte placed within it. The anode is immersed in the electrolyte and the form is surrounded with latex which carries the cathode. The negatively charged colloidal rubber particles are thus precipitated on the form. Sulfur, accelerators, and fillers are sometimes incorporated in the latex so that they will also be deposited with the rubber which can then be vulcanized later.

Several processes have been developed for concentrating latex before shipment. The most important are (1) separation of a more highly concentrated latex by centrifuging; (2) creaming by addition of glue, Iceland moss, or some other chemical capable of separating latex into two layers, one rich in rubber, the other poor; and (3) evaporation of water after addition of a hydrophilic substance capable of stabilizing an emulsion.

By the third process, a product known as "Revertex" is produced which contains as much as 80 per cent solids and which can be diluted to any desired concentration without precipitation.

It has also been found possible, by adding suitable emulsion-stabilizing agents, to vulcanize the rubber particles in latex before coagulation. Such a product is manufactured under the name "Vultex." The same process may also be applied to concentrated latices. The colloidal behavior of these vulcanized latices is the same as that of the unvulcanized suspensions. They may be precipitated either by a coagulating electrolyte or by electrodeposition to yield a continuous and strong film of vulcanized rubber.

Latex has also assumed importance in the manufacture of rubberized filaments and fabrics. For a given rubber content, latex is far less viscous than a benzene or toluene solution of rubber. Hence, fabric can be very satisfactorily rubberized by impregnation with latex. Addition of wetting agents enhances its value for this purpose.

Deproteinized Rubber

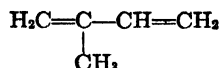
Most of the water-soluble components of latex remain in solution during coagulation. The resins and proteins, however, together with a portion of the water-soluble substances also, are carried down and are

therefore present in ordinary crude rubber. For most applications, the presence of these extraneous materials in small amounts is not detrimental. Indeed, they are often definitely advantageous in promoting vulcanization and improving the properties of the vulcanizates. For certain specialized uses, however, such as cable sheathing, where extreme water-resistance is essential, they may be troublesome.

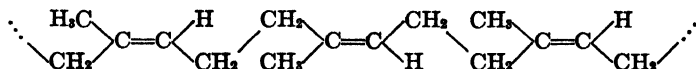
Several methods have been developed for deproteinizing rubber. Among them, the most effective one involves hydrolysis by addition of alkali and heating to about 50°. The proteinaceous degradation products are soluble in water and can be removed by subsequent dilution, coagulation, and washing, or by dialysis followed with coagulation and washing. Care must be observed to keep the temperature of hydrolysis as low as possible so that the rubber hydrocarbon will not be affected deleteriously. Deproteinized rubber is more readily oxidized than ordinary crude rubber and is somewhat less readily vulcanized. Whereas the nitrogen content of ordinary crude averages about 0.4 per cent, deproteinized rubber is available in which this figure has been reduced to 0.015 and even 0.006 per cent. In commerce, deproteinized rubber is distinguished by the slightly pink color imparted to it by purposeful addition of a trace of eosin.

Chemistry

Pyrolysis, ozonization, hydrogenation, and other reactions show that the rubber hydrocarbon is a linear 1,4-addition polymer of isoprene,



The average number of monomeric units present in a single polymeric molecule is still open to debate, but it is now commonly believed to be in the order of 4000 to 6000. A small segment of the rubber molecule may be represented as follows:

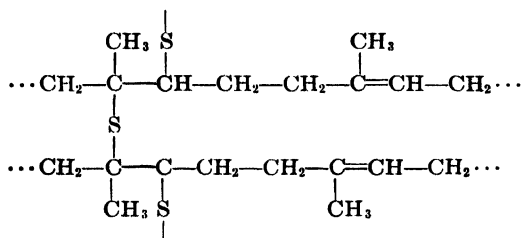


It will be noted that the *cis* configuration has been assigned to this formula; that is to say, both $-\text{CH}_2-$ groups attached to the unsaturated system of each C_5 unit are sterically arranged so that they are on the same side of the double bond. The *trans* form is thought to exist in the hydrocarbon components of balata and gutta percha, materials which are harder than rubber at room temperature, but which soften rather sharply at temperatures considerably below the gradual softening range of rubber.

The double bonds of rubber are reactive toward many chemical

agents, among which oxygen, chlorine, hydrogen chloride, and various isomerizing agents are industrially important. The effect of these chemicals is discussed in Chapter 21.

The chemical explanation of vulcanization still awaits clarification. One theory assumes the establishment of cross-linkages between chains of various rubber molecules by addition of sulfur at double bonds in a general manner like that illustrated below:



The result of vulcanization is thus formation of a tridimensional structure which is less susceptible to heat, possesses less tack, shows less cold flow or permanent set, and is stronger and more resistant to abrasion and to solvents than the initial raw rubber. The plasticity of raw rubber disappears upon vulcanization so that milling can no longer be carried out effectively.

It should be emphasized, however, that many of the phenomena associated with vulcanization are difficult to explain by the simple representation of the process just given. Numerous other theories of vulcanization have been propounded, but as yet none has been found more satisfactory.

Physical Properties

In the earlier general discussion of rubber-like substances, the elastic behavior of rubber was traced to the possibility of temporarily straightening out and aligning randomly kinked molecules by application of stress. It was also noted that the tensile strength of rubber, that is to say its resistance to deformation, increases with stretching because of the formation of microcrystallites.

Many of the physical properties of rubber are dependent upon the thermal and mechanical history of the material tested. Even its density varies between 0.912 and 0.934 at 20°, depending upon these factors. The refractive index of purified rubber at 20°, using the sodium D-ray, has been reported to be 1.5215 for smoked sheet, 1.5227 for crepe, and 1.5238 for Para rubber.

Rubber first swells, then dissolves in many aliphatic and aromatic hydrocarbons and chlorinated hydrocarbons, as well as in carbon di-

sulfide. Only solutions of low concentration can be obtained, for larger proportions of rubber yield gels. Ether divides rubber into two fractions called sol- and gel-forms, the first being soluble, the second insoluble in this solvent. These two forms of rubber can be converted into each other by various physical and chemical treatments.

Rubber can be broken down in molecular size by mechanical working on the mill. This phenomenon is reflected in greater solubility, increased ease of compounding with various ingredients, increased plasticity, and decreased viscosity of solutions of a given concentration. The last of these effects is shown graphically in Figure 226.

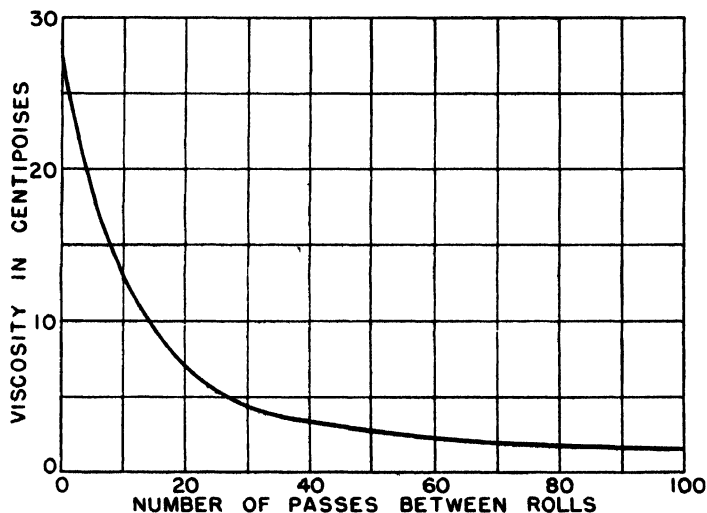


Figure 226. Effect of mastication upon the viscosity of crude rubber as determined in 1 per cent benzene solution at 25° some months after mastication. (*Dawson and Porritt* ^{27a})

Unvulcanized rubber can be stretched to many times its own length. Its degree of extensibility is greater than that of the vulcanized product. Both raw and cured rubber liberate heat upon being stretched, a phenomenon known as the Joule effect. Table 111 shows the magnitude of this effect in the case of smoked sheet.

Table 111. Heat Evolved on Stretching Smoked Sheet ^{27a, 27b}

Elongation %	80	186	361	428	621	658	821
Heat evolved g-cal/g rubber	0	0.84	2.33	2.86	4.58	5.24	6.80

On the removal of stress, a stretched piece of rubber partially returns to its original size and shape, but not completely. The difference be-

Table 112. Effects of Stretching Smoked Sheet Strips⁷⁰
(for 30 mins at 48°)

Elongation %	% Set after 10 days at room temperature	% Set after heating at 100° for 1 hr and cooling to room temperature, following a ten day relaxation period at room temperature
50	7.5	7.5
100	20	17.5
150	27.5	20
200	40	27.5
250	55	30
350	125	52.5
400	142.5	—

tween its initial length and its length 24 hours or more after release of stress is known as permanent set. This property, too, depends on the history of the rubber. Table 112 gives an indication of the permanent set of raw rubber under various conditions.

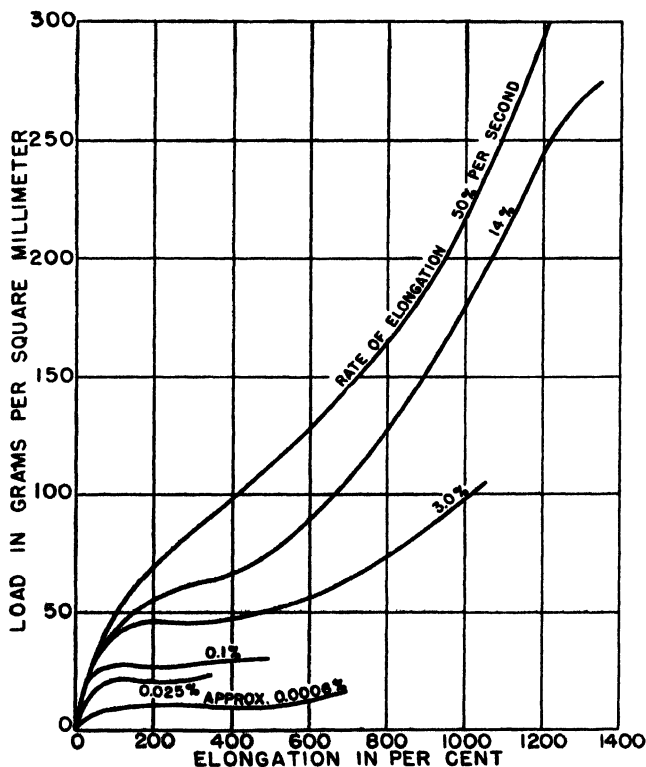


Figure 227. Influence of rate of elongation upon the stress-strain curve of raw natural rubber. (Adapted from Rosbaud and Schmid⁷⁴)

The tensile strength of raw rubber is dependent on numerous factors, including conditions of testing as well as history of the sample. The rate of elongation markedly influences the results obtained. This fact recalls previous statements that tensile strength increases with the development of crystallites on stretching, but that slow extension does not result in crystallization. The temperature of examination also affects the tensile strength of rubber. Vulcanization greatly decreases temperature susceptibility.

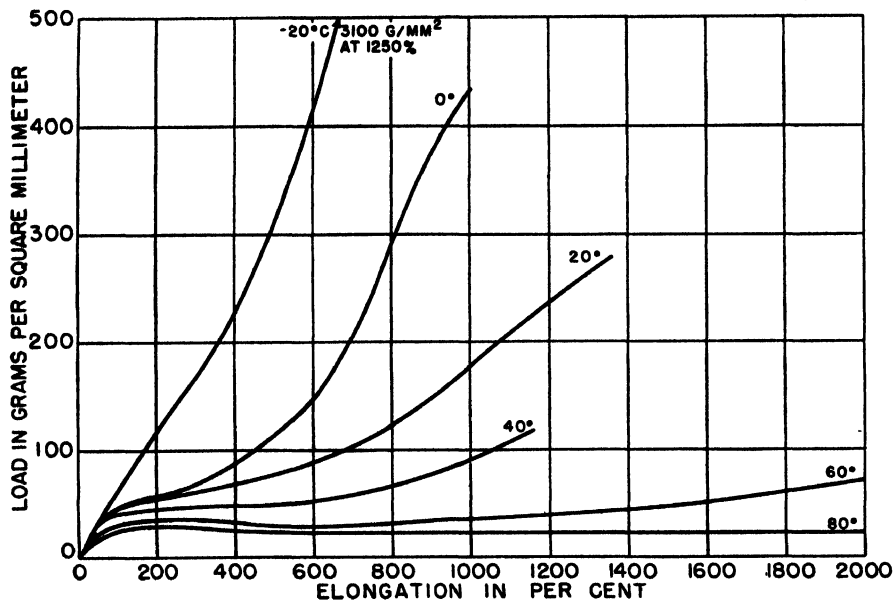


Figure 228. Influence of temperature on the stress-strain curve of natural raw rubber. (Rate of elongation: approximately 14 per cent per second.) (Rosbaud and Schmid ⁷⁴)

The physical properties of vulcanized rubber are subject to wide variation, depending on the details of compounding and curing. For the relationship between all of the many variables which can enter into the building of a rubber compound and the properties of the cured material, the reader is referred to specialized comprehensive treatises and tabulations, some of which are mentioned at the end of this chapter. For specific tests applied to rubber compounds, these sources should also be consulted.

The tensile strength of vulcanized rubber usually runs between 2500 and 4000 lbs per sq in, depending on formulation. Raw rubber may be as low as 150 lbs per sq in, the precise figure depending markedly on test conditions.

The solubility of vulcanized rubber is less than that of raw rubber. In general, swelling of a vulcanizate occurs without solution, although the strength is seriously impaired so that the rubber "rots."

Compounding and Curing

Only a very limited amount of rubber is utilized in the unvulcanized state—chiefly in cements and gummy masses for adhesive tapes. Even for these applications it is ordinarily masticated so that practically none is employed without treatment of some kind. Almost all rubber products, with these two exceptions, are vulcanized.

The compounding and vulcanization of rubber is a highly developed art. Many substances are used to control the properties of the finished article, while conditions of compounding and curing must be adjusted carefully according to the nature of the ingredients and the characteristics desired in the finished product.

Except in those specialized cases already discussed where latex is employed, it is essential to masticate the raw rubber for a short time before adding other ingredients. This operation not only ensures uniformity of the crude, but it also softens the rubber to a point where added materials may be milled into it homogeneously and it adjusts the plasticity of the rubber to that required for the contemplated method of fabrication, such as calendering or extrusion. The more the mastication, the greater is the degree of plasticity of the milled rubber. Various products require different degrees of plasticity. Both time and temperature must be controlled carefully. At 240° F the rate of breakdown in an internal mixer is at a minimum; both above and below this temperature, it is much faster. Various chemicals such as β -naphthyl mercaptan may be added to assist breakdown. On the other hand, such compounds as benzidine and *p*-aminophenol serve as stiffeners.

After mastication has reached the desired point, the other ingredients are added directly on the rubber mill or in the Banbury. The order of mixing is important. Sulfur is usually added last.

Numerous classes of materials are used in preparing a rubber compound. Not only raw rubber—smoked sheet, crepe, or Para—but also reclaim, factice (sulfurized drying oils), mineral rubbers (more or less elastic bituminous substances derived from Gilsonite and petroleum asphalts), and occasionally "AXF" for oil-resistant stocks (see Chapter 13) may be used as part of the elastomeric base material. Vulcanizing agents, accelerators, activators, antioxidants, and fillers are employed. Use of sun-checking inhibitors, plasticizers or softeners, odorants, and coloring pigments is common. Other special compounding ingredients may be needed at times.

Vulcanizing Agents

Thin rubber goods can be vulcanized at room temperature by treatment with the vapors of sulfur chloride or, according to the Peachey process, by alternate exposure to sulfur dioxide and hydrogen sulfide, whereupon elementary sulfur is liberated *in situ*.

The great majority of rubber goods, however, are produced by vulcanization with sulfur itself. Occasionally thiuramdisulfides serve both as accelerators and vulcanizing agents. Organic peroxides and nitrobenzene are capable of curing rubber, but are not employed industrially. Quinone dioxime has been developed by H. L. Fisher as a vulcanizing agent for specialty purposes. It is particularly effective in curing "Butyl" rubber. The amount of sulfur utilized in soft rubber goods normally runs from 0.5 to 4 per cent of the weight of crude rubber and is mixed in on rolls or in Banbury mixers. Vulcanization is usually carried out at temperatures within the range of 100 to 140°, although some compounds built with ultra accelerators can be cured at lower temperatures, even at room temperature. Dry heat, open steam, or closed molds may be used. Rubber hose is frequently cured within a temporary extruded lead sheath which is later removed.

Accelerators

Various inorganic oxides, especially zinc oxide, litharge, white lead, and magnesia, catalyze or "accelerate" vulcanization. It was fortunate indeed that Charles Goodyear's original experiment in which he discovered vulcanization was carried out in the presence of white lead. In 1906, Oenslager found that certain organic amines were also effective aids in facilitating cure. Since that time, several hundred organic compounds, more serviceable than metallic oxides, have been developed as accelerators. These substances do more than influence time of cure. They also affect tensile strength, elongation, tear resistance, and sometimes aging. In some cases they may shorten mixing time by their softening effect. Accelerators are commonly used in an amount equal to 0.5 to 1 per cent of the weight of raw rubber. Without them, several hours of heating at temperatures as high as 140° would be necessary to bring about vulcanization. Under such drastic curing conditions, many of the valuable physical properties of the vulcanizate would be impaired. Accelerators have the effect of shortening curing time and, often, of lowering the temperature. With some accelerators, curing time is critical, the effect of over-cure upon physical properties being as deleterious as under-cure. The best accelerators are those which do not cause impairment of properties if heating is carried beyond the point at which

optimum characteristics are first developed. Slow accelerators will bring about vulcanization of soft rubber in 1.5 to 2 hours at 140°. Rapid accelerators reduce the requisite time to 40 minutes, or less. Ultra accelerators cause vulcanization within a few minutes at temperatures even below 100° and at room temperature on several hours' standing.

Important current accelerators can be divided into four general groups:

- (1) *Condensation products of aldehydes with ammonia or organic amines* (moderately fast):

Hexamethylene tetramine ("Hexa")

Butyraldehyde-monobutyl amine ("833")

Formaldehyde-aniline ("A-10," "Formaline")

Acetaldehyde-aniline ("A-77," "R & H 50D")

Butyraldehyde-aniline ("A-32," "808," "Beutene")

Heptaldehyde-aniline ("Heptene")

Formaldehyde-*p*-toluidine ("8")

- (2) *Substituted guanidines* (moderately fast):

Diphenyl guanidine ("DPG")

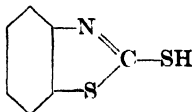
Di-*o*-tolyl guanidine ("DOTG")

Triphenyl guanidine ("TPG")

- (3) *Heterocyclic sulfur compounds* (fast):

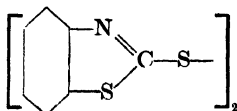
2-Mercapto-benzothiazole,

("Captax," "MBT," "Thiotax")



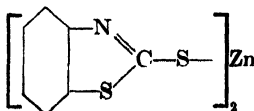
2,2'-Benzothiazyl disulfide,

("Altax," "MBTS," "Thiofide")



Zinc benzothiazyl sulfide,

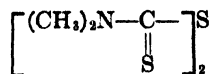
("OXAF," "Zenite")



- (4) *Thiurams and related derivatives of carbon disulfide* (ultra):

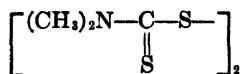
Tetramethylthiurammonosulfide,

("Monex," "Thionex")



Tetramethylthiuramdisulfide

("Methyl Tuads," "Thiuram M," "Tuex")

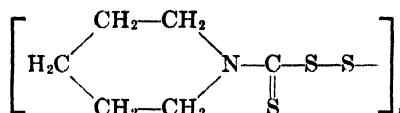


Tetraethylthiuramdisulfide

("Ethyl Tuads," "Thiuram E")

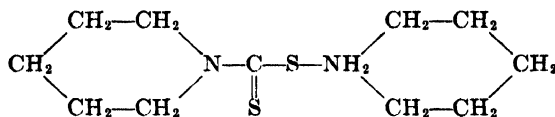
Di-N-pentamethylenethiuramtetrasulfide

("Tetrone A")



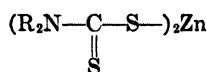
Piperidinium-N-pentamethylenedithiocarbamate

("552," "Pip-pip," "Naugatex 144")



Zinc salts of dimethyl-, diethyl-, dibutyl-, and dibenzyl-dithiocarbamates

(Respectively "Methasan," "Methazate," and "Methyl Zimate"; "Ethasan," "Ethazate," and "Ethyl Zimate"; "Butasan," "Butazate," and "Butyl Zimate"; and "Arazate.")



Lead dimethyldithiocarbamate ("Ledate")

Zinc butyl xanthate ("ZBX")

Activators

Accelerators should usually be activated. A number of inorganic materials exercise the ability to develop the full activity of vulcanization accelerators. Zinc oxide is the most important activator and is employed for this purpose in most rubber mixes in amounts ranging from 1 to 5 per cent of the weight of crude rubber. Some other metal oxides behave

similarly. Stearic acid, selenium, tellurium, and various amines also serve as activators. Stearic acid is required, for example, with "Captax."

Antioxidants

Antioxidants, used to the extent of about 1 per cent, are utilized to retard aging upon exposure to atmospheric oxygen. Common antioxidants include secondary aromatic amines, such as phenyl- α -naphthylamine ("Neozone A") and phenyl- β -naphthylamine ("Neozone D," "Age-rite Powder"), and condensation products of aldehydes or ketones with aromatic amines, such as "Age-rite Resin" derived from acetaldehyde and α -naphthylamine, "VGB" derived from acetaldehyde and aniline, and "BLE" obtained from acetone and diphenylamine.

Fillers

Many finely divided fillers are used in rubber compounding. Some of them are active reinforcing agents which greatly increase tensile strength and resistance to abrasion and tearing; others are more or less inactive insofar as their influence on ultimate physical properties is concerned, although the working characteristics of the compound prior to vulcanization are affected thereby. As in the plastics industry, although fillers may result in a less costly compounded article, this is not the primary reason for their use today.

Among the so-called "inert" fillers are whiting, diatomaceous earth, clays, barytes, slate flour, and talc.

The most important reinforcing agents are carbon black, zinc oxide, magnesium carbonate, blanc fixe, micronized calcium carbonate, and certain clays. Maximum reinforcement with carbon black usually occurs with 40–50 per cent of filler, based on rubber content. The most effective form of carbon is channel black, produced from natural gas by partial oxidation. Less active are the so-called "soft" or "Thermatomic" blacks made by pyrolysis of natural gas or petroleum fractions in the absence of air. Acetylene black is unique in imparting greater electrical conductivity to the vulcanizates than does carbon black. Channel blacks cause considerable stiffening of the vulcanized product, while soft blacks yield soft, resilient goods.

Softeners and Plasticizers

Softeners and plasticizers facilitate milling and fabricating operations. Vegetable and mineral oils, high-boiling aromatic hydrocarbon cuts, waxes, solid fatty acids like stearic acid, pine tar, pine oil, rosin, and coumarone-indene resins are used for this purpose.

Miscellaneous Compounding Ingredients

Besides representatives of the various classes already listed, numerous miscellaneous substances are compounded with rubber in order to produce special effects. In the manufacture of sponge rubber goods, for example, sodium bicarbonate or ammonium carbonate may be added as a bubble-forming or blowing agent. Organic compounds which decompose on heating to yield gaseous products are used for the same purpose, such as diazoaminobenzene. Fibrous fillers, especially cotton flock, may be used to impart leather-like characteristics to vulcanized rubber goods. Powdered metals such as aluminum are used where light reflection is desired, as in balloon fabric. Powdered lead may be compounded with rubber in order to make the vulcanizate resistant to x-rays, or sheet rubber may be laminated with lead foil for the same purpose. Phenolic resins, cashew nutshell oil resins, and asbestos are all compounded with rubber in the manufacture of various kinds of brake linings, while abrasives are incorporated with rubber in the manufacture of belts and wheels for grinding and polishing.

In order to give a specific idea of the diversity of materials employed in rubber compounding, typical formulas for tire treads and inner tubes are given in Tables 113 and 114.

Forms and Uses

Compounded rubber is fabricated in several ways. It may be molded, extruded, or calendered. It may be reinforced with cloth by friction calendering or spreading. Cloth- or wire-reinforced tubing can be constructed with special tubular weaving equipment. It may be electro-deposited or otherwise precipitated upon suitable forms either before vulcanization or afterwards. It can be used to coat or impregnate filaments and fabrics, either in solution form or as latex.

The most important civilian as well as military use of rubber is, of course, in the manufacture of tires for automobiles, trucks, airplanes, jeeps, and numerous other vehicles. A related application is in the production of tank treads. Before Pearl Harbor, about 77 per cent of the rubber consumed in this country went into tires and tire products. An automobile tire is a complex combination of rubber, cord, and metal bead wire. Its construction represents a complicated assembly of several fabricating processes, brought to a high state of perfection by modern methods of mass production.

Numerous rubber articles are grouped together under the general term of mechanical goods. About 10 per cent of pre-Pearl Harbor rubber

Table 113. Tread Compounds for Passenger Tires ¹⁰³

	First Grade	Second Grade	Third Grade
Smoked Sheet	100	88	72.5
Reclaim, Whole Tire	—	22	50
"Reogen" (softener)	2	1.5	1.5
Stearic Acid	3	3	3
Pine Tar	1	1.5	1.5
"Age Rite Hipar" (antioxidant)	1	1	1
"Age Rite Resin D" (antioxidant)	1	1	—
Zinc Oxide	3	3	3
Carbon Black	47.5	42.5	37.5
Sulfur	3	2.875	2.875
"Captax" (accelerator)	1	0.8	0.7
	162.5	167.175	173.575

Cure at 274° F for 50 minutes

Table 114. Passenger Inner Tube Compounds ¹⁰³

	Black	Red
Smoked Sheet	100	58
Reclaim, Red Tube	—	46
"Reogen" (softener)	1	2
Paraffin	1	1
Stearic Acid	1	—
"Age Rite Resin D"	2	—
Zinc Oxide	3	3
"P-33" ("Thermatomic" carbon)	40	—
"Kalite No. 1" (coated calcium carbonate)	—	20
Red Iron Oxide	—	4
Sulfur	1.5	1.25
"Captax" (accelerator)	0.75	—
"Altax" (accelerator)	0.75	1.2
"Zimate" (or "Tuads") (accelerator)	0.15	0.125
	151.15	136.575

Cure at 307° F for 4 minutes

went into the construction of mechanicals, including such diverse products as belting, hose, packing, rollers, molded goods, matting, tubing, and sponge rubber. Wire and cable insulation, footwear, and proofed fabrics represent other important outlets for rubber. American consumption of rubber by principal products in 1937 is shown in Table 115.

A complete list of specific applications of rubber in modern living would be well nigh impossible. When one contemplates its absolute necessity in 20th Century civilization it is difficult to realize that before 1839—the year of discovery of vulcanization—no such material as cured rubber was known to man! It is equally extraordinary that only recently have other materials been developed which could challenge its undisputed monopoly!

Table 115. Rubber Consumption in the United States, by Principal Products, 1937¹¹

	Long Tons	Per Cent of Total
Pneumatic casings	333,867	62.88
Inner tubes	51,450	9.69
Solid and cushion tires	1,653	0.31
Boots and shoes	20,214	3.81
Heels, soles, and slab soling	13,176	2.48
Rubberized fabrics, rubberized clothing (finished), and bathing caps and bathing suits	10,524	1.98
Mechanical rubber goods, rubber flooring, rubber mats and matting	56,422	10.63
Hard-rubber goods	3,660	0.69
Rubber thread, cement, and gloves	9,514	1.79
Tire sundries, repair materials, rebuilt or retreaded tires, and camelback	11,115	2.09
Other products, including drug and medical sundries, balloons, stationers' bands, erasers, golf and tennis balls, toys, and sponge-rubber products	19,374	3.65
Total	530,969	100.00

Hard Rubber

In modern practice, the amount of sulfur used for making soft rubber goods rarely exceeds 4 per cent. Before organic accelerators were developed to their present state of perfection, as much as 8 to 10 per cent of sulfur was sometimes employed. Where more than this amount is used, soft resilient characteristics begin to disappear and the vulcanizate approaches hard rubber or ebonite. Products containing between about 8 and 25 per cent of sulfur are unstable. They are, moreover, too hard to be of service in soft rubber goods and yet too soft to be of use as hard rubber. In practice, it has been found that the valuable physical properties of hard rubber are not well developed until the amount of combined sulfur approaches that theoretically required to attain full saturation of the double bonds. This theoretical value is 47 per cent of the weight of rubber reacted therewith or 32 per cent of the total weight of ebonite produced.

The lower limit of utility of hard rubber goods is about 25 per cent combined sulfur. As the percentage increases from this figure, hardness and heat resistance are improved to the detriment of impact and tensile strengths. It is commonly supposed that as the amount of sulfur is increased, the unsaturation of the rubber molecule is decreased by formation of more and more sulfur bridges between the double bonds of different molecules. The netting index of hard rubber is therefore relatively high. The rubber chains are mechanically restrained and the normal elasticity of rubber disappears entirely.

Hard rubber is a moldable semi-synthetic plastic of the chemosetting type.

Most accelerators do not materially increase the speed of vulcanization of rubber beyond the soft rubber stage. The reaction, however, is exothermic and must be controlled with care in order to prevent excessive temperature rise during the early stages, with consequent scorching and formation of blow holes. Several hours are usually required for complete cure to ebonite. Hard rubber dust is the most important filler. It is used in most hard rubber goods, its function being primarily to decrease the amount of hydrogen sulfide liberated during vulcanization. Coloring pigments and other fillers are sometimes added as well.

Hard rubber can be cured under little or no pressure although 500 to 1000 lbs per sq in is preferred during the early stages. It is easily machined.

Hard rubber is resistant to water up to about 140° F. Above that temperature it begins to swell and distort. It is resistant to aqueous solutions of most inorganic salts, acids, and bases, but is attacked by many organic solvents such as aromatic hydrocarbons, chlorinated hydrocarbons, carbon disulfide, ether, acetone, and aniline. Typical physical properties of two commercial grades of hard rubber are listed in Table 116.

Table 116. Physical Properties of Hard Rubber *

	"Ace"	"Banner"
Color	jet black	black
Finish (when polished)	high luster	fair luster
Specific gravity	1.15 to 1.20	1.20 to 1.25
Tensile strength (lbs/sq in)	6500 to 9000	4000 to 7000
Elongation (%)	8 to 3	6 to 2
Softening temperature (under load)	130 to 140° F	130 to 140° F
Transverse strength (lbs/sq in)	12,000 to 15,000	9000 to 12,000
Compressive strength (lbs/sq in)	11,000 to 12,000	10,000 to 11,000
Coefficient of linear expansion (per ° F)	0.000035	0.000035
Dielectric strength (specimen 0.15 to 0.25 mm thick; volts/mm)	65,000	40,000
Dielectric constant (1000 cycles at 5 volts)	2.9 to 3.1	3.3 to 3.5
Phase difference (1000 cycles)	0.25 to 0.30°	0.30 to 0.40°
Resistivity (megohm—cm)		
Volume	over 10 ⁸	over 10 ⁸
Surface		
(50% humidity)	10 ⁸	10 ⁸
(84% humidity)	5 × 10 ⁵	5 × 10 ⁵
Moisture absorption (in air, 90% relative humidity, room temperature, 24 hrs)	0.018%	0.02%

* Manufacturers' data. American Hard Rubber Company.

Typical applications of hard rubber include sliding door frames, rails, and safety stops for display refrigerators, glazing strips, dehydrating

tubes, bunker lids, doors, water lubricated bearings, storage battery containers and separators, funnels, jars, sheets, rods, and tubes, valves, gears, pump and water meter pistons, telegraph and telephone parts, electrical insulating equipment, and pipe fittings. Hard rubber is also used in lining metal equipment such as vats and tanks, tank cars, conduits, pumps, and reaction vessels.

Seamless hard rubber coverings can be produced upon irregular metal articles by the anode process involving electrodeposition and subsequent vulcanization.

Prices for top quality rod stock, unfinished, normally average 80 to 85 cents per pound in quantity.

SYNTHETIC RUBBER

History

According to the Goebelsian affirmations of the German Chemist, Harries, it was he who first produced synthetic rubber and who made all the important discoveries in this domain of modern science and technology. In several articles he proclaimed his omniscience and in 1913 devoted twelve pages of the *Annalen* to a discussion of the work of chemists in other lands, attempting to prove that they were all false prophets. Despite Harries' bombastic claims, even a cursory glance at the literature reveals the fact that the first fundamental discoveries in this field were made by French, English, and Russian chemists. Because of shortages of the natural product, however, Germany was forced to manufacture an inferior synthetic during World War I. To that country, therefore, goes the dubious honor of first commercializing a low grade substitute.

Numerous chemists in various countries had subjected rubber to pyrolysis during the first half of the last century, but it was not until 1860 that the Englishman, Greville Williams, isolated and identified isoprene among the products of its destructive distillation. It was also he who named isoprene. A few years later, in 1875, the French chemist, G. Bouchardat, obtained this diolefin in considerable quantity by pyrolysis of rubber. He was the first to suggest that rubber is a high polymer of isoprene. Four years later he described the formation of the first synthetic rubber, made from isoprene by treatment with fuming hydrochloric acid followed by removal of liquid hydrogen chloride addition products by distillation. According to Bouchardat, the solid residue, which amounted to about one-sixth of the isoprene used, possessed "the elasticity and other properties of rubber itself."

In 1882 the English chemist, Sir William Tilden, polymerized isoprene

to a rubber-like compound with nitrosyl chloride. Two years later he obtained the diolefin by pyrogenetic decomposition of turpentine, thus effecting the first synthesis of a rubber-like material from non-rubber sources. In 1892, he gave a more complete description of rubber-like polymers of isoprene derived from turpentine and stated that this "artificial rubber unites with sulfur in the same way as ordinary rubber, forming a tough, elastic compound." He was thus first to produce a vulcanized synthetic rubber.

In 1901, the Russian chemist, Ivan Kondakoff, obtained a rubber-like polymer from 2,3-dimethyl-butadiene. This material was the methyl rubber produced in Germany during World War I, but its discovery was Russian in origin. In 1910 another Russian chemist, Lebedev, reported the polymerization of butadiene to a rubber-like material. Outstanding early investigations of synthetic rubber were also carried out by the Russian, Ostromislenski. It is perhaps worthy of note that the first book on synthetic rubber was published in Russian about 1913.

In 1912, Sir William Henry Perkin, Jr., and a group of associated British chemists, especially Strange and Matthews, who had undertaken a comprehensive study of this field, proposed both isoprene and butadiene as sources of synthetic rubber. They suggested various means for producing these diolefins. One synthesis of butadiene started with *n*-butanol. The Fernbach fermentation process for the manufacture of butyl alcohol and acetone was developed at the Pasteur Institute in Paris as an associated project of this investigation and became a fruitful commercial venture and, indeed, military necessity years before synthetic rubber reached maturity. Of especial interest was the proposed method of synthesis of butadiene from alcohol through acetaldehyde, aldol, and 1,3-butylene glycol. The glycol was then dehydrated to the diene or converted to the corresponding dihalide and dehydrohalogenated. Coincidentally and independently, in 1910, these English workers and Harries in Germany discovered the utility of sodium as a catalyst for converting diolefins to synthetic rubbers.

All of this work preceded World War I. Spurred on by the newly created demand for rubber in automobile tires and by a \$3-per-pound-price for the natural product, industrial firms in both England and Germany attempted to develop a commercially useful grade of synthetic. Although much progress was made, the products were not satisfactory and work was abandoned in both countries upon the outbreak of hostilities. During the war, however, the blockade had a telling effect on Germany and it became necessary for her to undertake synthetic production. By 1918, methyl rubber from 2,3-dimethyl-butadiene was being manufactured at the rate of about 150 tons per month. It cost about

30 marks per kilogram. A total of 2350 tons of methyl rubber was produced before the end of the war. Two additional plants having an annual capacity of 8000 tons were under construction at the time of the Armistice. Most of this methyl rubber was used in hard rubber articles, especially battery boxes of submarines. Some was also utilized in tire manufacture, especially in solid tires, but their life was limited. These products might have been considerably better had modern methods of rubber compounding then been known. Commercial production of methyl rubber ceased at the close of the war.

About the middle of the 'twenties, research on synthetic rubbers was undertaken in earnest by the I. G. in Germany and the du Pont Company in the United States. The former organization concentrated on the polymerization of butadiene, at first with a sodium catalyst (Natrium—whence the word Buna) and subsequently in aqueous emulsion with other catalysts. Numerous copolymerizable monomers were tried and two—acrylonitrile and styrene—were found especially meritorious. Out of this work during the 'thirties came the numbered Bunas (straight butadiene polymers), Buna N (an acrylonitrile copolymer), and Buna S (a styrene copolymer).

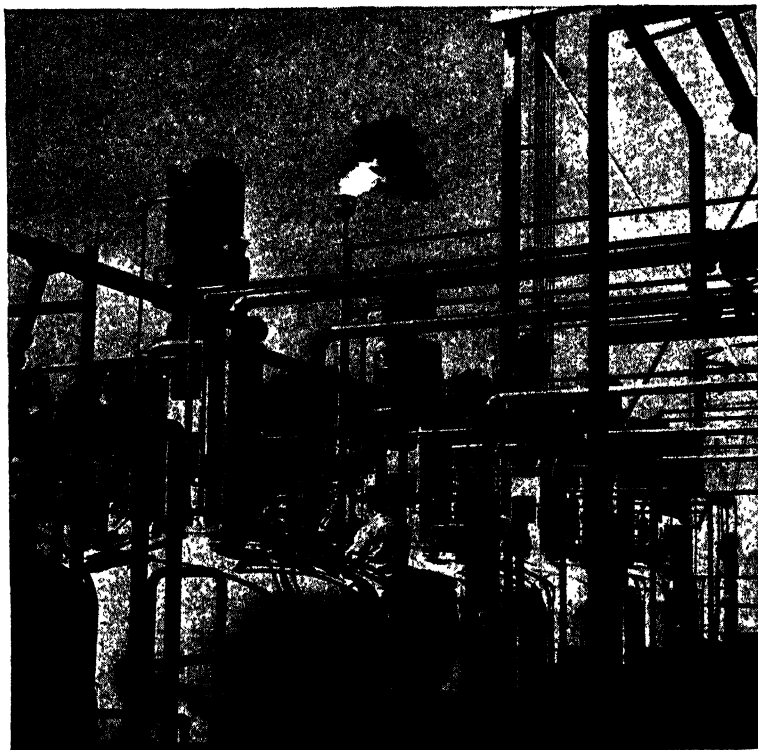
In the meantime the du Pont Company had developed neoprene by polymerization of 2-chlorobutadiene, called chloroprene. This synthetic was the outgrowth of work done at the Experimental Station in Wilmington under W. H. Carothers, following along lines of investigation initially opened at Notre Dame University by Father J. A. Nieuwland. Neoprene, first called by the trade-marked name, "Duprene," was announced in 1931 and was the earliest successful synthetic rubber of the diolefin polymer type to be produced anywhere in the world—with the possible exception of Russia where the status of the synthetic rubber industry has been ambiguous.

A year previously, in 1930, another American synthetic was placed on the market; namely, "Thiokol." This material differed substantially from the diolefin polymers in that it was a condensation product of ethylene dichloride and sodium polysulfide. Its manufacture was the result of researches of a Kansas City chemist, J. C. Patrick, who began his investigations in this field in 1921, initially with the idea of trying to produce an automobile antifreeze.

The commercial production of both "Thiokol" and neoprene preceded the German manufacture of "Buna" rubbers. The American and German developments followed divergent paths. The domestic products were introduced because of oil resistance and other unique properties which they possessed that are not found in natural rubber. Although "Buna N," later called "Perbunan," is oil-resistant, the greatest amount of in-

terest in Germany centered around "Buna S" which was evolved purely as a rubber substitute with an eye to the future military position of that nation.

During the 'thirties, Russia developed "Sovprene," an analog of neoprene, and the SK rubbers—butadiene polymers lettered A or B to denote their origin from petroleum or alcohol, respectively.



Courtesy United States Rubber Co.

Figure 229. A view of the reactor area at the Naugatuck synthetic rubber plant operated for the Government by United States Rubber Company at Naugatuck, Conn. Ground was broken for the plant before Pearl Harbor, in September 1941. It was placed in operation a year later.

By 1941 appreciable amounts of "Perbunan" had been imported into this country and used because of oil resistance. Several American firms had begun to enter into the production of butadiene-acrylonitrile copolymers, the first one being announced by Goodrich under the name "Hycar OR." The Standard Oil Co. of New Jersey soon followed with American production of "Perbunan" under agreements with the I. G.

Meanwhile, the manufacture of neoprene and "Thiokol" had become

well established. The rubber-like characteristics of properly plasticized polyvinyl chloride were being utilized in "Koroseal" and "Tygon," while polyvinyl alcohol had come into limited use as a water-sensitive, but extremely oil-resistant rubber-like product called "Resistoflex."

Then came Pearl Harbor and the rapid succession of events which eliminated most of the Far Eastern rubber supply of this country. The fantastic scramble to manufacture huge amounts of synthetic rubber in



Courtesy United States Rubber Co.

Figure 230. General view of the Institute synthetic rubber plant operated for the Government by United States Rubber Company at Institute, W. Va. This was the first of the large integrated synthetic rubber plants to get into production. The plant for making monomers was operated by Carbide and Carbon.

the United States to replace the natural product is now a matter of history. War-time production estimates of 1944 are listed below in appropriate sections. "Buna" S, the most important item in this program, was not previously produced in the United States. "Butyl" rubber, an important part of the program, was first announced in 1941. Processes had to be developed and plants constructed for this mammoth undertaking within less than three years. Tables 117 and 119 show the location of synthetic rubber plants in this country.

Classification

The expression "synthetic rubber" is an unfortunate misnomer which has become so commonly accepted that there seems slight hope of universally replacing it by the more meaningful term "elastomer" * pro-

* Exception can be taken to the word "elastomer" on etymological grounds because of the fact that intrinsically it does not convey the meaning given to it. It is derived from the Greek *elastikos* (to drive) and *meros* (part). The word "mer"

posed by H. L. Fisher. No truly synthetic rubber has yet been produced. According to Fisher's scheme the principal commercial elastomers now manufactured can be classified as follows:

- I. Elastoprenes
 - (A) Butadiene polymers and copolymers
 - (B) Chloroprene polymers and copolymers
- II. Elastolenes
 - (A) Olefin polymers and copolymers of substantially saturated nature
- III. Elastothiomers
 - (A) Organic polysulfides
- IV. Elastoplastics
 - (A) Plasticized vinyl polymers
 - (B) Plasticized ethyl cellulose
 - (C) Polymethyl acrylate
 - (D) Flexible alkyds, including polyesters of dimerized drying oil acids
 - (E) Polyarylene ethylenes ("AXF")

The various types of elastoplastics listed above have already been discussed at appropriate points in this text. The remainder of this chapter is therefore devoted only to a consideration of the elastoprenes, elastolenes, and elastothiomers.

Elastoprenes

Polymers and Copolymers of Butadiene

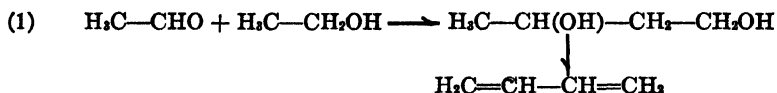
Raw materials.

Butadiene. Butadiene is the essential intermediate required for manufacture of all the elastoprenes save polychloroprene. It may be polymerized either alone or in combination with acrylonitrile, styrene, or isobutylene. The synthetic rubber program has required the rapid development of facilities for producing enormous volumes of this diolefin.

Itself has also been used by Carothers to designate the individual unit of repetition in both addition and condensation polymers (as distinguished from the monomeric substances themselves from which the polymer is produced). Strict etymological accuracy would lead to the expression "elastopolymer" and the various classes of elastopolymers would, in turn, become "elastopolyprenes," "elastopolyenes," and "elastopolythiomers." These terms, however, are cumbersome. The expressions suggested by Fisher are sufficiently abbreviated to make for ease of use and they have been accepted in chemical circles. Barron has proposed the term "elastics" to cover all rubber-like materials, both natural and synthetic, "elastomers" to be confined to Fisher's "polyprenes," "elastenes" as equivalent to Fisher's "elastolenes," "ethenoids" for materials based on the polyvinyl grouping, "thioplasts" instead of "elastothiomers," and "elastoplasts" in place of "elastoplastics."

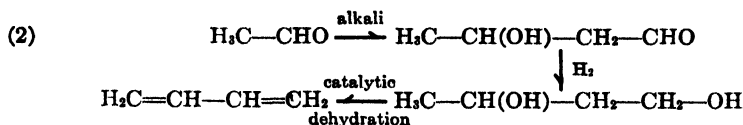
The plants making it, like those producing most of the styrene required for GR-S and the synthetic rubber (polymerization) plants themselves have been operated for the government by various private companies on a cost-plus-fixed-fee basis.

Butadiene, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$, is gaseous at room temperature, boiling at -4.6° and freezing at -108.9° . Its limits of flame propagation in admixture with air are 2 to 11.5 per cent by volume of hydrocarbon. Butadiene can be obtained by a very large number of chemical reactions. One of the earliest processes was developed by the Russian chemist, Ostromislenski, who was awarded a large monetary prize by his government in 1915 because of its discovery. It involved pyrolysis of a mixture of acetaldehyde and ethyl alcohol, according to the following equations:

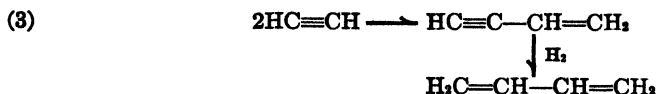


Ten years later this method was modified by Lebedev who developed into commercial proportions a process for the direct conversion of ethyl alcohol to the diolefin by pyrolysis. More recently, a portion of Russian butadiene has been derived from petroleum.

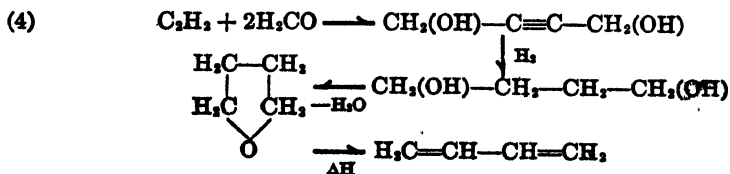
In Germany, butadiene has been produced from acetylene by way of acetaldehyde which was then converted to the diolefinic hydrocarbon by the following series of reactions:



Considerable research has been done abroad upon dimerization of acetylene and reduction of the resultant vinyl acetylene:



During World War II, butadiene was also manufactured in Germany from formaldehyde and acetylene in order to conserve the latter. This process involved intermediate synthesis of butinediol and tetrahydrofuran, in accordance with the following series of reactions:



Tetrahydrofuran was not necessarily isolated in this process, although it was also produced as an intermediate for the synthesis of other resins, notably nylon.

In the United States, butadiene is manufactured from alcohol, petroleum, and natural gas. Both synthetic and fermentation alcohol is employed. All three basic materials are converted to the diolefin by suitable



Courtesy Hycar Chemical Co.

Figure 231. Cracking plant for the production of butadiene from petroleum.

combination of pyrolytic and catalytic operations which involve separation of unreacted raw material and recycling. The 1944 annual rated production of butadiene in this country, according to raw materials, is given below:

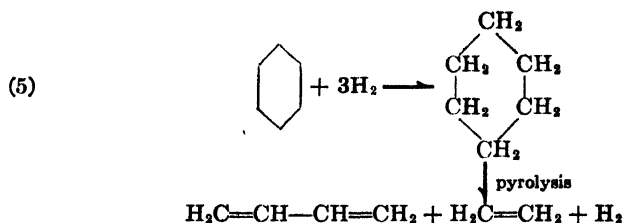
Alcohol	230,000 short tons
Butylene	290,000 short tons
Butane	75,000 short tons
Naphtha cracking (so-called "refinery conversion")	<u>95,400 short tons</u>
Total	690,400 short tons

Butadiene was first produced commercially in this country only a few years ago and was made by dehydrohalogenating 2,3-dichlorobutane. It

is doubtful whether this process can compete successfully with newer methods.

Work has also been carried out on the dehydration of 2,3-butylene glycol obtained from grain by means of a special fermentation process using *Aerobacter aerogenes*. Conversion is about 90 per cent complete after forty hours. This process is not of much industrial significance at present, although several laboratories have investigated its possibilities.

Another method for producing butadiene was at the point of translation into plant operation when it became necessary to discontinue development because of wartime shortages of benzene. It involves the following series of reactions:

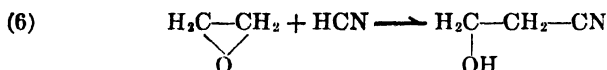


One of the most serious problems in the manufacture of butadiene for the production of commercial elastoprenes lies in its purification. Traces of certain impurities, even of some closely similar hydrocarbons, are sufficient to vitiate the quality of copolymers produced therefrom. They may hinder or even stop copolymerization.

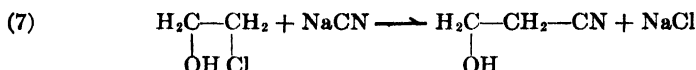
Styrene. The production of styrene has already been discussed in Chapter 16. Pyrolysis of ethylbenzene is the process universally employed at present. Isopropylbenzene, or cumene, is reported to give better yields, but demands for this aromatic hydrocarbon in high octane aviation gasoline have precluded its use for this purpose. Ethylbenzene may be produced by ethylation of benzene by means of either ethyl alcohol or ethylene. Other processes are known, but are not economically feasible. Ethyl alcohol (95%) can be reacted with benzene at temperatures in the order of 600° F and in the presence of solid catalysts containing phosphoric acid. Nitration-grade, sulfur-free benzene must be used in this process and both reactants must be recycled to obtain good yields. The Dow process for the manufacture of ethylbenzene involves reaction of benzene with ethylene at 190° F under 15 pounds gage pressure. Aluminum chloride is used as catalyst. Benzene of 2° F boiling range may be used and it is not necessary that it be sulfur-free. Hydrocarbon mixtures, rather than pure ethylene, may be used even where the ethylene concentration is as low as 38 per cent, provided they be propylene-free. Yields are nearly theoretical, polyethylbenzenes formed dur-

ing reaction being subsequently dealkylated to the monoethyl compound. Ethylbenzene is then dehydrogenated by pyrolysis of the preheated vapor admixed with highly superheated steam. The styrene is purified by fractional distillation, sulfur being added to prevent polymerization in the still. Stabilization of styrene polymers is effected by incorporation of about one part of *t*-butylcatechol with 20,000 parts of monomeric styrene. 1944 annual rated capacity of styrene plants in this country was 202,700 short tons.

Acrylonitrile. Acrylonitrile is produced by dehydration of ethylene cyanohydrin. The latter compound is prepared either by reaction of hydrogen cyanide with ethylene oxide,



or by metathesis between sodium cyanide and ethylene chlorohydrin,



Equation (6) represents the process principally used at present.

Recently the Sinclair Refining Company has developed a method for manufacture of nitriles which appears to involve catalytic reaction of ammonia and various hydrocarbons. Acrylonitrile is now available from the Harshaw Chemical Co. as a result of this work.

Table 117 gives a summary of the wartime status of plants producing intermediates for butadiene elastoprenes.

Manufacture of Polymers. Butadiene can be polymerized alone to elastomeric analogs of rubber. A segment of the polymer thus formed may be represented inadequately by the formula



Some cross-linking appears to occur as a result of 1,2-addition during polymerization. Products of this type have not thus far appeared generally on the American market, but they have been manufactured for over ten years in Russia under the designations "SKA" and "SKB" and for several years in Germany under the names "Buna" 85 and "Buna" 115. A pilot plant was in operation for their production in Poland at the time of the German invasion of that country, the synthetic being known as "Ker." In the manufacture of all of these products, sodium was employed as catalyst. The molecular weights of the German products, as determined by viscosity methods, were 85,000 and 115,000, respectively; production of the numbered "Bunas" was reported to have ceased shortly after the beginning of World War II.

Table 117. Planned 1944 Status of Butadiene, Styrene, and Acrylonitrile Production ⁽¹⁾

Company	Rated Annual Capacity	Location
Butadiene Plants		
<i>Northeast</i>		
Koppers United Company ⁽²⁾	80,000 short tons	Pittsburgh, Pa.
Carbide & Carbon Chemicals Corp. ⁽²⁾	80,000 " "	Institute, W. Va.
Carbide & Carbon Chemicals Corp. ⁽²⁾	60,000 " "	Louisville, Ky.
Polymer Corp., Ltd. ⁽²⁾	30,000 " "	Sarnia, Ont.
Sun Oil Co. ⁽⁴⁾	15,000 " "	Toledo, O.
Publicker Commercial Alcohol Co. ⁽²⁾	10,000 " "	Philadelphia, Pa.
Carbide & Carbon Chemicals Corp. ⁽²⁾	5,000 " "	Charleston, W. Va.
Regional total	280,000 " "	
<i>Southwest</i>		
Neches Butane Products Co. ⁽³⁾	100,000 " "	Port Neches, Texas
Cities Service Oil Co. ⁽³⁾	55,000 " "	Lake Charles, La.
Sinclair Rubber, Inc. ⁽³⁾	50,000 " "	Houston, Texas
Phillips Petroleum Co. ⁽⁴⁾	45,000 " "	Borger, Texas
Standard Oil Co. of La. ⁽³⁾ , ⁽⁵⁾	28,400 " "	Baton Rouge, La.
Humble Oil & Refining Co. ⁽³⁾	30,000 " "	Baytown, Texas
Eastern States Petroleum and Refining Co. ⁽⁵⁾	12,800 " "	Houston, Texas
Humble Oil & Refining Co. ⁽⁵⁾	7,000 " "	Ingleside, Texas
Lion Oil & Refining Co. ⁽⁵⁾	6,700 " "	El Dorado, Texas
Taylor Refining Co. ⁽⁵⁾	5,500 " "	Corpus Christi, Texas
Regional total	340,400 " "	
<i>Pacific Coast</i>		
Shell Chemical Co. ⁽³⁾	25,000 " "	Torrence, Calif.
Southern Cal. Gas Co. ⁽⁵⁾	30,000 " "	Los Angeles, Calif.
Standard Oil Co. of Calif. ⁽⁴⁾	15,000 " "	El Segundo, Calif.
Regional total	70,000 " "	
Grand Total	690,400 " "	
Styrene Plants		
<i>Northeast</i>		
Koppers United Co.	37,500 short tons	Pittsburgh, Pa.
Carbide & Carbon Chemicals Corp.	25,000 " "	Institute, W. Va.
Dow Chemical Co.	10,000 " "	Sarnia, Ont.
Dow Chemical Co.	4,200 " "	Midland, Mich.
Regional total	76,700 " "	
<i>Southwest</i>		
Monsanto Chemical Co.	51,000 " "	Texas City, Texas
Dow Chemical Co.	50,000 " "	Velasco, Texas
Regional total	101,000 " "	
<i>Pacific Coast</i>		
Dow Chemical Co.	25,000 " "	Los Angeles, Calif.
Grand Total	202,700 " "	
Acrylonitrile Plants		
<i>Northeast</i>		
American Cyanamid Co.	—	Linden, N. J.
Rohm & Haas Co.	—	Bristol, Pa.

⁽¹⁾ Compiled by B. H. Weil from data contained in the brochure on synthetic rubber accompanying *Chem. Met. Eng.* for Nov. 1943, supplemented from other sources. According to U.S. Tariff Commission preliminary figures, actual 1944 production totals were $1,212.8 \times 10^6$ lbs of butadiene and 349.4×10^6 lbs of styrene. Approximately 10×10^6 lbs of acrylonitrile was consumed in 1944 production of "Buna" N type elastomers.

⁽²⁾ Plants producing butadiene from alcohol.

⁽³⁾ Plants producing butadiene from butylenes.

⁽⁴⁾ Plants producing butadiene from butane.

⁽⁵⁾ Plants producing butadiene from cracking processes (including "refinery conversion" processes of that nature).

Copolymers of butadiene with styrene and acrylonitrile are now the important elastoprenes manufactured in both Germany and the United States, the former very much the more important, the latter being produced especially because of oil-resisting characteristics. Both of these general types of copolymers are made by polymerizing an aqueous emulsion of the mixed monomers. Proportions of the unsaturated materials, as well as the emulsifying agents and catalysts can be varied within rather wide limits. Although copolymerization can be effected in 4 to 5 days at room temperature, commercial practice is to operate under slightly elevated pressure at temperatures between 45 and 60°, under which conditions polymerization occurs within a few hours. The general formulation of emulsions for copolymerization is given in Table 118. The presence of certain inorganic salts, some even in traces, is said to be deleterious to polymerization.

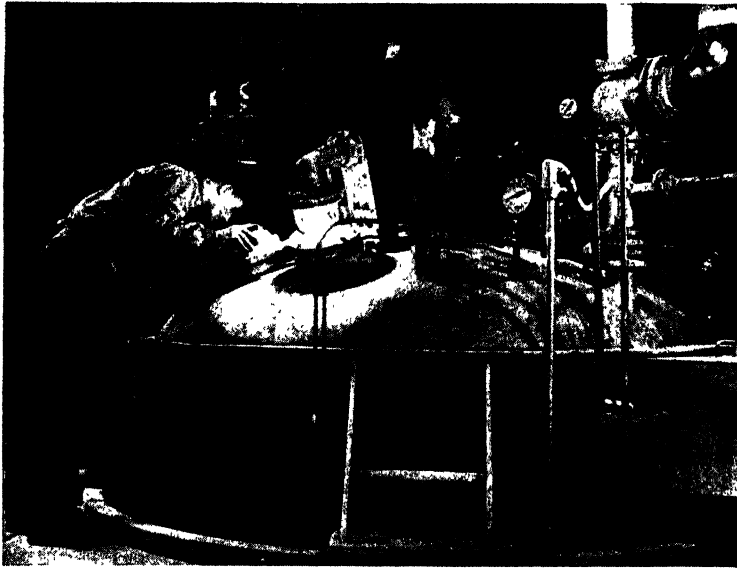
Table 118. General Formula for Emulsion Polymerization ⁴¹

50-75	Butadiene
50-25	Styrene or acrylonitrile
1-5	Emulsifying agent (soap, sodium alkyl sulfate, alkylaryl sulfonate, etc.)
1-5	Buffer (sodium acetate or sodium phosphate)
0.1-1	Polymerization catalyst (hydrogen peroxide, potassium persulfate, or preferably sodium perborate)
100-400	Water

The usual butadiene/styrene or acrylonitrile ratio is about 3/1.

Emulsion polymerization yields a latex which must be coagulated by addition of salt and acids or, occasionally, acetone or alcohol. Oxidation of the coagulum is prevented by incorporation therein of about 2 per cent of phenyl- β -naphthylamine. Except for special purposes, no effort is made to remove emulsifying agents (usually soap) carried down by precipitation; these materials may amount to 4 per cent or more of the weight of elastomer.

Properties and Uses. The butadiene elastoprenes behave in much the same manner as natural rubber. They are, in general, compounded with the same ingredients and in about the same proportions. There are certain differences between these synthetics and natural rubber, however, both chemically and physically. Whereas natural rubber is strictly a linear polymer, these synthetics appear to be cross-linked to some extent. Despite the fact that interlinear bridges are relatively few, they exercise an influence on physical and chemical properties. The synthetics are more resistant to oxidation than natural rubber. They are less readily broken down on the mill (whence longer times of mastication), less tacky (especially after mastication), and, in the vulcanized form, show a



Courtesy United States Rubber Co.

Figure 232. Reactor in which butadiene and styrene are copolymerized. To make 90,000 long tons of GR-S annually, the Institute Plant requires 6 units of 12 reactors each.



Courtesy United States Rubber Co.

Figure 233. After polymerization, the batch is drawn off into "blow-down" tanks where reaction is stopped. Unreacted monomers are then recovered.



Courtesy United States Rubber Co.

Figure 234. Condenser for recovery of butadiene at the Institute Plant.



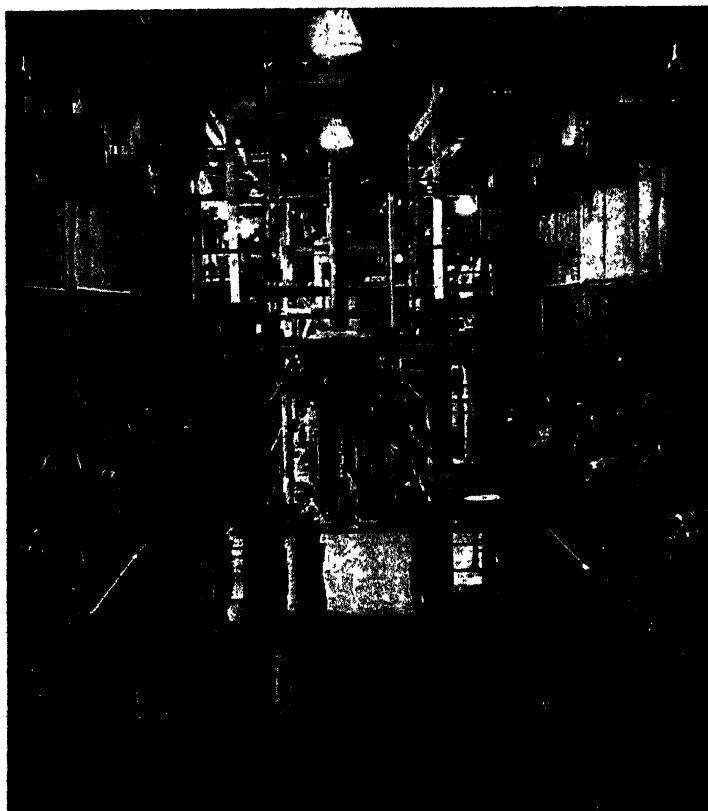
Courtesy United States Rubber Co.

Figure 235. Batches of GR-S latex are bulked and blended in twelve 30,000-gallon storage tanks at the Institute Plant. Here an operator draws latex from the blending tanks and discharges it to other tanks where it will be creamed and the rubber content coagulated.



Courtesy United States Rubber Co.

Figure 236. Filtered GR-S at the Institute Plant.

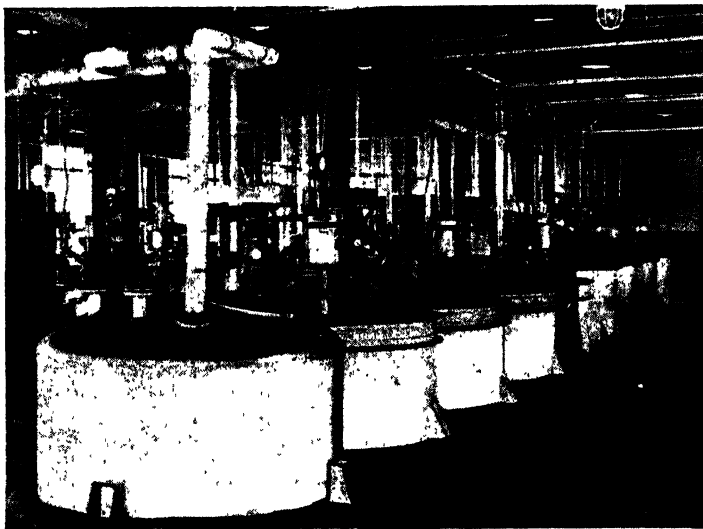


Courtesy United States Rubber Co.

Figure 237. GR-S is dried in twelve large 3-pass driers at the Institute Plant. At full operation these driers will evaporate 160 tons of water every day for the annual capacity of 90,000 long tons of GR-S.

greater propensity toward heat build-up where fabricated into automobile tires. All of these properties can be traced, in part, to the presence of cross-linkages in the molecular structure of the materials.

The amount of vulcanizable unsaturation in butadiene elastoprenes is less than in natural rubber; hence, the amount of sulfur required for complete vulcanization is less. Polymers of butadiene and copolymers of butadiene with both styrene and acrylonitrile can be cured with a large amount of sulfur to yield products resembling hard rubber. This family of elastoprenes differs from all of the others now manufactured in this respect; they are the only ones capable of yielding a highly cross-

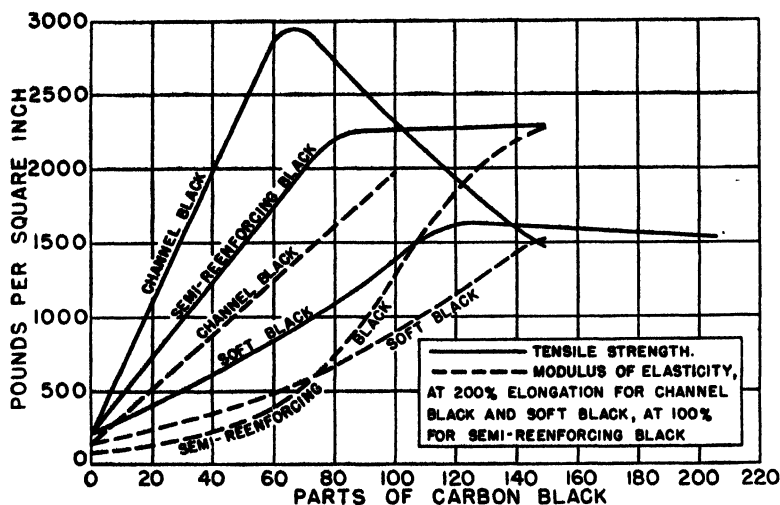


Courtesy Hycar Chemical Co.

Figure 238. Battery of polymerizers used in the production of "Hycar" latex.

linked, hard-vulcanized material. In all instances, these products possess superior heat and solvent resistance as compared with ebonite from natural rubber.

A vast amount of research has been carried out on the compounding of the butadiene elastoprenes. While the general principles are similar to those employed in the case of natural rubber, it is common practice to mill for a longer time, using a masticating agent such as dodecyl mercaptan or xylyl mercaptan. The effect of carbon black is even more pronounced than in the case of natural rubber. Figure 239 shows the influence on modulus and tensile strength of various types of carbon black compounded with "Buna" S.



Courtesy E. I. du Pont de Nemours & Co. Rubber Chemicals Division 35

Figure 239. Effect of carbon black on the modulus of elasticity and tensile strength of GR-S vulcanizates. Cure: 30 minutes at 287° F.

Base formula:	GR-S	100.0
	Sulfur	2.0
	Stearic acid	1.0
	Zinc oxide	5.0
	"Thionex"	0.5
	Carbon black	As required

In 1944 copolymers of styrene and butadiene were scheduled for production chiefly in government owned plants operated by private industry as shown in Table 119.

Government rubber produced by copolymerization of butadiene and styrene is designated GR-S. Trade names of styrene copolymers manufactured by private industry include "Buna" S, "Chemigum" IV, "Hycar" OS, "Hycar" EP, and "Hycar" TT.

GR-S is the product which was selected to serve as general replacement for natural rubber. Properly compounded GR-S resembles natural rubber in most properties, including elasticity, strength and abrasion characteristics. Like natural rubber, it lacks oil-resistance. It is less satisfactory than natural rubber in some respects, especially because of the increased time of mastication required for breakdown, lack of tack with consequent troubles encountered in tire building, and heat build-up through hysteresis—a serious factor in heavy duty tires, especially, because of its deleterious effect on the cord. It is less resistant to tearing and less resistant to low temperatures than natural rubber. These points of inferiority are, in most instances, not unduly serious and are being

Table 119. Copolymer Plants *

<i>Northeast</i>			
United States Rubber Co.	90,000	long tons	Institute, W. Va.
B. F. Goodrich Co.	60,000	" "	Louisville, Ky.
Firestone Tire & Rubber Co.	30,000	" "	Akron, O.
Goodyear Tire & Rubber Co.	30,000	" "	Akron, O.
United States Rubber Co.	30,000	" "	Naugatuck, Conn.
National Synthetic Rubber Corp.	30,000	" "	Louisville, Ky.
Polymer Corp., Ltd.	34,000	" "	Sarnia, Ont.
Regional total	304,000	" "	
<i>Southwest</i>			
B. F. Goodrich Co.	60,000	" "	Port Neches, Texas
Firestone Tire & Rubber Co.	60,000	" "	Port Neches, Texas
Firestone Tire & Rubber Co.	60,000	" "	Lake Charles, La.
Goodyear Tire & Rubber Co.	60,000	" "	Houston, Texas
B. F. Goodrich Co.	45,000	" "	Borger, Texas
Copolymer Corp.	30,000	" "	Baton Rouge, La.
General Tire & Rubber Co.	30,000	" "	Baytown, Texas
Regional total	345,000	" "	
<i>Pacific Coast</i>			
Goodyear Tire & Rubber Co.	60,000	" "	Los Angeles, Calif.
United States Rubber Co.	30,000	" "	Los Angeles, Calif.
Regional total	90,000	" "	
<i>Grand Total</i>	739,000	" "	

* Compiled by B. H. Weil from data contained in the brochure on synthetic rubber accompanying *Chem. Met. Eng.* for Nov. 1943, supplemented from other sources. According to U.S. Tariff Commission preliminary figures, the actual 1944 total production of GR-S type synthetic rubber was $1,497.8 \times 10^6$ lbs in government plants and 3.2×10^6 lbs in private plants.



Figure 240. Lifting a completed ice grip tire made with GR-S from the mold.

Courtesy The Goodyear
Tire & Rubber Co.

studied intensively. Lack of tack can be overcome by incorporation of a few per cent of a new resinous tackifier made by General Aniline & Film Corp. under the name "Koresin." This product is a polymer of vinyl *p*-ter-butyl phenol, made by catalytic reaction of acetylene with the corresponding alkylated phenol. In German practice zinc or cadmium salts of organic acids have been utilized as catalysts. Tack developed by painting GR-S carbon black stock with hexane solutions of "Koresin" is at an optimum where the solution contains about 3 per cent of this polymer, as shown by Figure 241.

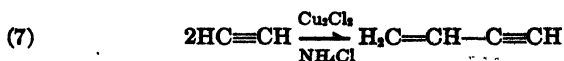
Estimates of maximum-efficiency-manufacturing-costs of GR-S have been given as about 20 cents per pound.

Butadiene-acrylonitrile copolymers have been manufactured chiefly by private industry under the trade names "Buna" N, "Perbunan," "Perbunan" Extra, "Chemigum" III, "Hycar" OR-15, "Hycar" OR-25, and formerly, "Thiokol" RD. These products sell at a premium price, in the order of 50 cents per pound and are especially useful because of their oil-resistant characteristics. A small amount of this type of elastomer has also been produced as GR-A under Government auspices.

Various other butadiene copolymers have been studied, but they are not yet in production. The Eastern Regional Research Laboratory has investigated copolymers with methyl acrylate and its analogs. To products of this character, the name "Lactoprene" has been applied because of the derivation of methyl acrylate from lactic acid. The Mathieson Alkali Co. has announced a new elastomer, reported to be unique in low heat build-up, made by copolymerization of butadiene with a dichloro-styrene.

Polymers and Copolymers of Chloroprene

Neoprene, originally trade-marked "Duprene," was the first elastoprene to be a commercial success. It was developed at the du Pont Experimental Station as an outgrowth of fundamental studies upon acetylene carried out by Father J. A. Nieuwland and his students at Notre Dame University. Nieuwland found this hydrocarbon capable of undergoing polymerization by passage through an aqueous solution of cuprous and ammonium chlorides. The dimer: vinylacetylene, and the trimer: divinylacetylene, are formed simultaneously according to the following equations:



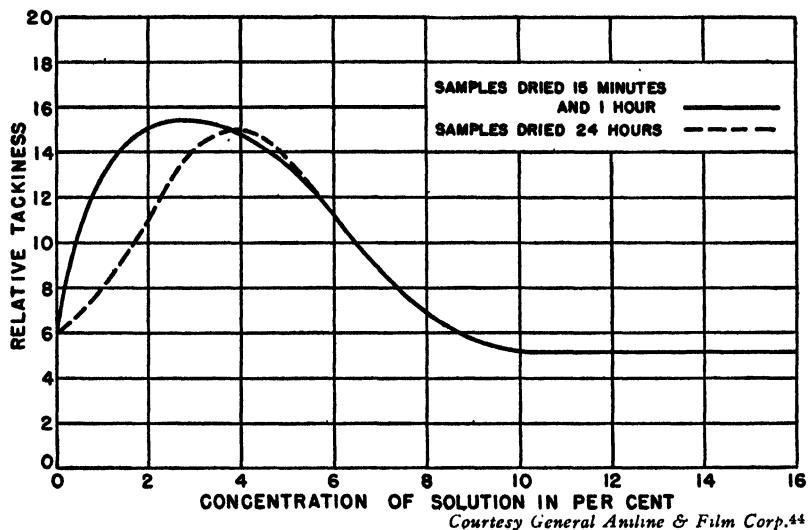


Figure 241. Tackiness of GR-S carbon black stock painted with solutions of "Koresin" in hexane. (Tack determined by means of the General Aniline & Film Corporation method; cf. Ref. 44.)



Courtesy Hycar Chemical Co.

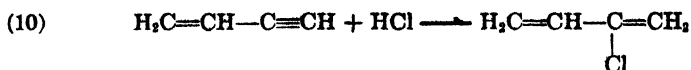
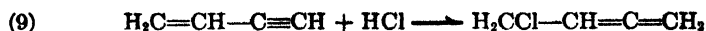
Figure 242. Extrusion of a "Hycar" compound through a laboratory tubing machine.

The first of these products is the intermediate used in manufacture of neoprene; the second, a by-product, can be converted to a liquid known as "S-D-O" which resembles drying oils.

"S-D-O." Divinylacetylene is usually obtained in greater amount than vinylacetylene unless conditions are carefully controlled. Even then it is produced in appreciable quantities as a by-product. Inasmuch as vinylacetylene is the commercial source of neoprene, divinylacetylene is an industrial by-product. On standing, this hydrocarbon absorbs oxygen from the air and becomes dangerously explosive. Warmed in the absence of air, it polymerizes to a highly unsaturated viscous liquid which, on further heating, yields a hard, insoluble resin. On exposure of a film of the intermediate oil to the atmosphere, it dries rapidly, giving a protective coating which is highly impervious to moisture. The oil is known under the trade designation "S-D-O," meaning synthetic drying oil. Because of the explosion hazard involved in storage and use, "S-D-O" has had a precarious industrial career and has been withdrawn from general distribution. It can be used to waterproof concrete and other types of walls which are prone to pass moisture, but inasmuch as it does not exhibit good adhesive characteristics, it should be employed only on rough surfaces where mechanical anchorage prevails. "S-D-O" surface coatings are liable to fail under repeated vibration.

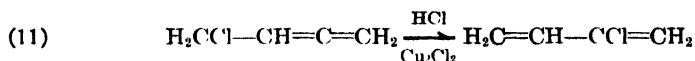
Neoprene. Monovinyl acetylene, b.p.: 5° , is the essential intermediate in the synthesis of neoprene. Its preparation is carried out under carefully controlled conditions in order to hold divinylacetylene formation to a minimum.

Vinylacetylene polymerizes, on standing, to a viscous oil and finally to a hard, resinous solid. In many reactions this dimer of acetylene behaves like a conjugated diolefin. This character is of especial commercial significance in the case of addition of hydrogen chloride. On shaking with concentrated hydrochloric acid, in the absence of other chemicals and at room temperature, vinylacetylene gives 4-chloro-1,2-butadiene in good yield, together with lesser amounts of the isomeric 2-chloro-1,3-butadiene.



In a typical reaction, Carothers and his coworkers found these two compounds present in the ratio of 2.2/1 after 7 hours of shaking at room temperature, reaction then being 43 per cent complete. Various water-soluble salts catalyze these reactions. In some instances, as with calcium

chloride, the two chlorinated products are formed in the same ratio as in the absence of catalyst, the effect of the salt being simply to increase the rate of reaction. In other cases, especially that of cuprous chloride, rearrangement of the 4-chloro- into the 2-chloro-isomer apparently occurs and the product is entirely the latter. 4-Chloro-1,2-butadiene can be quantitatively rearranged to the corresponding 2-chloro-1,3-butadiene by means of the same catalysts. This fact is not surprising in view of the presence of both the allyl and allene configurations in the primary chloride. These two isomers, however, are not tautomeric as in the case of many allyl systems, for the secondary halide possesses a halogen attached to an unsaturated carbon atom. Such a structure is conventionally very stable and rearrangement to the primary chloride, therefore, does not take place.

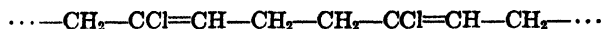


There is a marked difference between these two isomeric chlorides in their ease of polymerization. 4-Chloro-1,2-butadiene fails to polymerize on standing for several months, on distilling, or on heating at 50° under 6000 atmospheres for 45 hours. 2-Chloro-1,3-butadiene polymerizes readily, on the other hand. Indeed, Carothers has reported that its polymerization in bulk occurs some 700 times faster than that of isoprene.

By analogy with isoprene, 2-chloro-1,3-butadiene has been dubbed "chloroprene." It is a volatile, colorless liquid boiling at 59.4° and having a density at 20°/4° of 0.958. Its odor is reminiscent of ethyl chloride. Although its commercial significance lies in its ability to polymerize to a rubber-like polymer to be described shortly, chloroprene is capable of yielding several other different types of polymers. Cyclic dimers, known as β -polychloroprenes, are produced at temperatures of 60° or more in the absence of air. In structure, these β -polymers resemble terpenes obtained by dimerization of isoprene. They possess a marked odor and it is to their presence in small amount that the characteristic penetrating odor of the earlier types of neoprene has been traced. Under other conditions granular (so-called ω -) polymers are obtained and under still others, a balata-like polymer has been isolated.

If spontaneous polymerization at temperatures up to about 35° is stopped short of completion by precipitation with alcohol or coagulation by other means, a thermoplastic, so-called α -polymer is obtained which resembles milled smoked sheet rubber in many of its physical and mechanical properties. Except for certain copolymers, commercial neoprene consists of α -polychloroprene. It can be handled on a mill like rubber itself and is soluble in aromatic hydrocarbons. This α -polymer

is thought to possess a symmetrical linear chain, a segment of which may be represented as follows:



Both its symmetry and its linear character are indicated by the x-ray diffraction patterns of stretched polymer. It is one of the few synthetic rubbers which give crystalline x-ray diffraction patterns in the stretched state. In this respect it resembles natural rubber, methyl rubber, and polyisobutylene, but is in contrast to the butadiene-type synthetics which are thought to be somewhat cross-linked. Probably because of its strictly linear character, neoprene handles on the mill more like rubber itself than like the "Buna" rubbers.

Oxygen, peroxides, and irradiation catalyze the formation of α -polychloroprene.

The earliest grades of neoprene were produced from the monomer without the use of either solvent or modifying agent, save about 2 per cent of a stabilizer, such as phenyl- β -naphthylamine. For several years the principal grade of neoprene was manufactured by mass polymerization. More recently, emulsion polymerization methods have been employed. The properties of the emulsion polymer are superior with respect to color, odor, and milling characteristics. Emulsion polymers are more readily plasticized by the incorporation of small amounts of a variety of organic compounds. The emulsion polymer is available in several grades which differ largely with respect to processing characteristics.

In the manufacture of all but a few specialty grades, chloroprene is polymerized in aqueous emulsion and subsequently coagulated by freezing on a chilled revolving drum. A thin continuous film of coagulum is thus obtained and removed by means of a doctor blade. The film is thoroughly washed on an endless belt and oven dried, a process which eliminates odoriferous contaminants as well as water. The film is subsequently roped and cut into short lengths; or it may be shipped in milled sheets.

If the spontaneous polymerization of liquid chloroprene is allowed to proceed to completion, an elastic polymer, called μ -polychloroprene, is obtained. It begins to appear after polymerization of the monomer has proceeded to the extent of 30 to 40 per cent. It is for this reason that the α -polymer is produced commercially by stopping polymerization short of completion. The μ -polymer is also obtained where α -polychloroprene is allowed to stand for some time at room temperature. Conversion of α - to μ - form is accelerated by heat. At 130°, for example, transformation is complete in five minutes, whereas, at 30°, some ten days are required.

μ -Polychloroprene is thought to be formed as the result of cross-linking of chains of α -polymer, probably through establishment of direct carbon-to-carbon bonds. The transformation resembles the vulcanization of rubber in the physical development of elasticity at the expense of plasticity. This is the process which is brought about industrially during the curing of neoprene.

α -Polychloroprene cures spontaneously on standing. In order to prevent this loss of plasticity and make possible its compounding in accordance with the general principles of rubber technology it is necessary to stabilize the α -polymer. Secondary aromatic amines, especially phenyl- β -naphthylamine, inhibit vulcanization at normal temperatures making it possible to store α -polymer over long periods of time. This inhibiting effect begins to disappear at temperatures above 100° and stabilized α -polychloroprene compositions are usually vulcanized by heating at or above 115°.

Various substances act as catalysts or accelerators of vulcanization. Zinc oxide, zinc chloride, ferric chloride, and primary aromatic amines are among materials of this category, zinc oxide being especially useful in commercial practice. Polyhydric phenols like resorcinol, catechol, and pyrogallol act as ultra accelerators. Sulfur does not serve as a vulcanizing agent, but with certain types of neoprene it does act as an accelerator. It is recommended for use with neoprene where adhesion to brass plate is desired and to impart certain valuable properties to the vulcanizate.

Neoprene can be handled on rubber machinery much like natural rubber. It can be mixed with the customary compounding ingredients, although their effect is usually not the same as with natural rubber. For a detailed discussion of compounding practice, trade publications should be consulted. It may be mentioned, however, that carbon black and zinc oxide exercise some reinforcing action, although not as much as with natural rubber. Whiting and clays often improve tear resistance. Zinc oxide and litharge serve as accelerators. Sulfur is sometimes used for the same purpose. Magnesium oxide prevents scorching. Rosin and various chemical plasticizers are used as softening agents, depending on the type of neoprene. Over-cure of neoprene does not result in marked deterioration of physical properties as is often the case with natural rubber.

Vulcanized neoprene is superior to natural rubber in solvent resistance, in retention of tensile strength after being swelled by such solvents as aromatic hydrocarbons, in resistance to heat, and in resistance to light, ozone, and oxidation in general. Where used in conjunction with the proper compounding ingredients, its vulcanizates possess relatively high non-flammability. As in the case of other elastoprenes, the properties

of vulcanized neoprene can be varied within wide limits by suitable compounding. Without added materials, μ -polychloroprene is colorless or light yellow where carefully prepared in the absence of oxygen. It is darker in color if polymerization occurs in the presence of considerable air or oxygen. At 20° its density is 1.23 and its refractive index (n_D^{20}) is 1.5512. It elongates about 800 per cent before breaking and shows a tensile strength of at least 2000 lbs per sq in at the breaking point. It swells, but does not dissolve in carbon tetrachloride, carbon disulfide, benzene, nitrobenzene, pyridine, aniline, ethyl acetate, and ether. Its resistance to gasoline and lubricating oils is much greater than that of natural rubber and its tensile strength is much less affected thereby.

Polychloroprene is produced commercially as several different grades of neoprene. An all-purpose type and a number of specialty grades are manufactured. The principal differences which exist among the several types of neoprene are concerned with the properties of the unvulcanized polymer and the processing operations to which they are suited. A stabilized aqueous emulsion of polychloroprene is marketed as neoprene latex, which is available in concentrations of 50 per cent and 60 per cent by weight of dry solids.

Copolymers of chloroprene with other polymerizable materials, such as acrylonitrile, isoprene, and styrene, have been made. The properties of these copolymers differ somewhat from those of the chloroprene polymers.

Neoprene and neoprene latex are produced in a privately owned du Pont plant at Deepwater, N. J. During the war, neoprene (GR-M) was produced in a government plant at Louisville, Ky.

Elastolenes

Fisher originally proposed the term elastolene to cover elastomers like polyisobutylene which are formed in the presence of catalysts like boron trifluoride. The word has been shortened to elastene by Barron and defined to include those elastomers which are substantially saturated polymers and copolymers of olefinic hydrocarbons. In this group Barron placed polyethylene, polyisobutylene, "Butyl" rubber, and "A-X-F." The last-named product has been discussed in Chapter 13. It differs from the other materials mentioned in that it is a Friedel-Crafts condensation product of aromatic hydrocarbons and aliphatic dihalides; hence its inclusion among the elastolenes is open to some question. Other plastics of recent origin which appear to qualify as elastolenes are sold under the trade names "Styraloy" and "Pliolite" S-3.

Elastomeric polymers and copolymers of methyl acrylate, classified in this text as elastoplastics, might also be considered as elastolenes derived from substituted olefins.

Polyethylene

The simplest elastolene in point of view of structure is polyethylene. Practically, however, the manufacture of this product presents many obstacles which have only recently been surmounted, so that this polymer is among the newer American plastics. Its development is a British achievement. Imperial Chemical Industries, Ltd., began its manufacture on a pilot plant scale early in 1939. When the war broke out in September of that year, English imports of German polyvinyl chloride for electrical insulating applications were, of course, cut off and this new plastic played a vital role in helping to relieve a difficult situation. Its manufacture in the United States on a pilot plant scale began in 1942. It is now produced by the Carbide and Carbon Chemicals Corp. and by the du Pont Company. The product of Imperial Chemical Industries is known under the trade name "Alkathene." Carbide's product is known as polyethylene DYNH resin; du Pont's as "Polythene." I.C.I. has also used the term "Polythene."

Chemistry. The structure of the product is apparently that of a paraffinic hydrocarbon of formula $-(CH_2)_n-$. Molecular weight of commercial polymers varies from 3000 to 50,000, several grades being produced in England, but only relatively high molecular weight material being manufactured in this country at present. Like other linear, symmetrical high polymers, polyethylene is largely microcrystalline in character, being composed of clusters* of orthorhombic crystals. Because of its crystalline nature it can be cold-stretched up to about 400 per cent. The tensile strength of sheets and filaments can be improved in this manner. Although elongation is normally irreversible, partial reversion can be made to occur by heating to temperatures of about 100°.

The methods employed for American manufacture of polyethylene have not been disclosed. According to a basic early British patent of the I.C.I., polymerization of ethylene to solid products is contingent on four conditions.

(1) High pressures must be employed—at least 500 atmospheres in the presence of oxygen or 1200 in its absence. The relation of molecular weight of polymer to pressure is shown in Table 120.

Table 120. Relation of Pressure to Molecular Weight of Polyethylene**
(Conditions: 0.06% oxygen, 200°, steel autoclave)

Pressure	Molecular Weight
520 atmospheres	2,000
1,000 "	4,000
1,500 "	6,000-12,000
3,000 "	12,000-24,000

(2) Temperatures of 100 to 300° are requisite, preferably 150 to 250°. Increasing temperature accelerates reaction, but lowers molecular weight so that at high temperatures grease-like products are obtained.

(3) Because of the exothermic character of the reaction, heat must be removed rapidly in order to avoid excessive temperature rise. For every pressure/oxygen-content ratio, there exists a critical temperature above which explosive decomposition of the ethylene occurs instead of polymerization. At 1500 atmospheres and 0.1 per cent oxygen, for example, this critical temperature is about 400°.

(4) The oxygen content, if any, must be held within carefully controlled limits. Under 1500 atmospheres and temperatures of 180 to 200°, the relation of yield and molecular weight to oxygen content is shown in Table 121.

Table 121. Relation of Oxygen Content to Formation of Polyethylene**

Oxygen Content (%)	Yield (%)	Molecular Weight
0.01	6	18,000
0.04	9	12,000
0.07	10	10,000
0.13	15	6,000
0.16	Explosive decomposition	

In the absence of oxygen, reaction occurs slowly over a period of several hours; in its presence, polymerization takes place quickly, but yields are lower. Continuous operation, however, can be set up in the presence of oxygen, unused ethylene being recycled. The oxygen consumed during reaction exerts a negligible effect on most of the chemical and physical properties of the polymer. The power factor, however, is increased by even traces of oxygen, so that electronic applications require minimal oxidation.

Properties. Polyethylene is supplied primarily in the form of a granular powder for molding and extrusion. It contains a small amount of added antioxidant and is of a grayish-blue translucence, opaque in thick sections. Uncompounded, it possesses a white translucence very similar to that of paraffin wax which it also resembles in feel. Although somewhat harder than wax—its Brinell is 2—it can be scratched with the fingernail. In other properties, however, such as toughness, flexibility, and strength, polyethylene differs markedly from the waxes. In thin sections it possesses a high degree of flexibility. Film and tape, for example, fabricated from unplasticized polyethylene are as limp and flexible as plasticized vinyl sheeting. Molded articles, however, of thick cross-section are rigid. Tubing and cable insulation possess varying flexibility, depending on thickness. Flexibility can be increased without

appreciable sacrifice of electrical properties or moisture resistance by compounding with the polybutenes. Its flexibility and toughness without ready extensibility are reminiscent of gutta percha and are retained over a considerable temperature range. Even at -45° thin strips (0.075 in thick) can be bent suddenly and sharply without breaking. Up to 90° polyethylene exhibits good recovery from deformation with

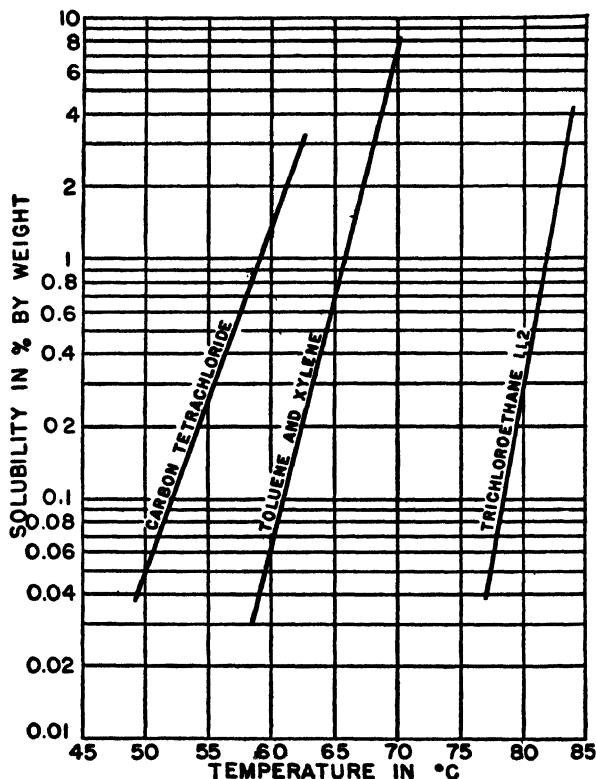


Figure 243. Solubility of polyethylene in organic solvents versus temperature. (Carbide and Carbon Chemicals Corporation Resin DYNH.) (Myers⁶⁶)

only very slight cold flow. It differs from most moldable thermoplastics in that it possesses a fairly sharp softening point in the neighborhood of 110° . It is flammable, burning slowly with a light blue flame.

Its tensile strength increases with molecular weight, as shown in Table 122.

The resistance of polyethylene to water and moisture is unexcelled. Its water vapor transmissivity at 25° is 0.4 gram per sq in per 24 hrs for sheeting 0.004 in thick and 0.07 gram for 0.010 in thickness. Its

Table 122. Tensile Strength of "Alkathene" *

Material		Tensile Strength (kgs/cm ²)	Ball and Ring Softening Point (°C)	Approximate Viscosity at 190° C (Poises)	Approximate Average Molecular Weight
"Alkathene"	2	160	115	35,000	19,000
"	7	140	112	10,000	17,000
"	20	120	110	3,500	15,000
"	70	100	106	1,000	13,000
"	200	80	100	350	—

* Adapted from manufacturers' data, Imperial Chemical Industries, Ltd., Plastics Division, London. (Cf. ³²)

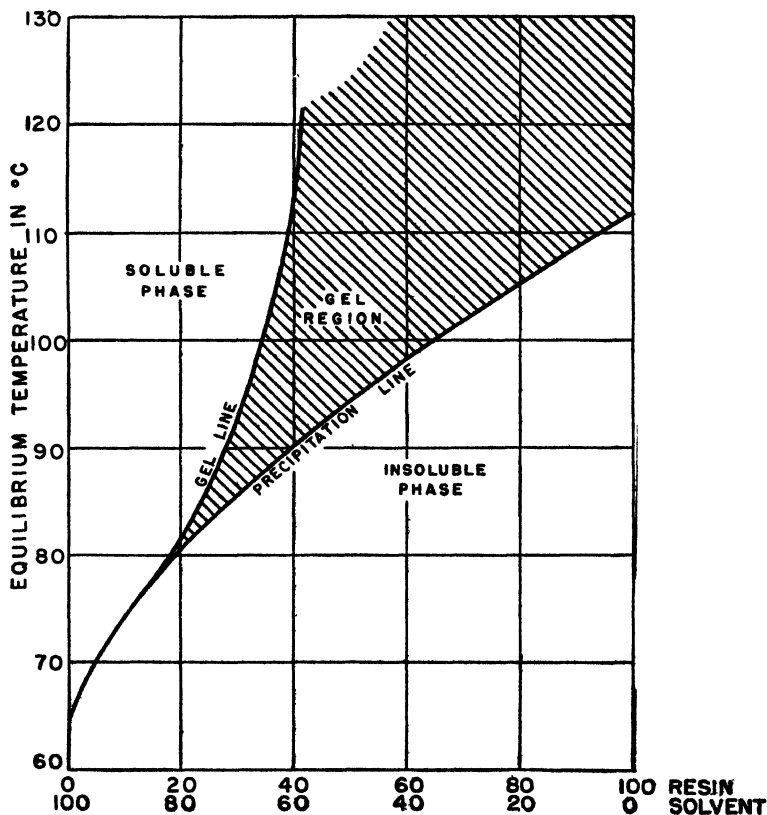


Figure 244. Phase diagram for polyethylene resin-xylene system. Concentration of resin in solvent, by weight per cent, versus equilibrium temperature. (Myers⁶⁰)

electrical properties are equally outstanding. It possesses the lowest density of any moldable rigid plastic, namely: 0.92–0.93 at 20°.

Polyethylene is incompatible with most thermoplastics, but can be compounded with natural and synthetic rubbers, gutta percha, polyisobutylene, and paraffin wax. The polybutenes improve flexibility. It can be filled with various pigments by milling at temperatures of 115° or above. Carbon black reinforces and stiffens it somewhat; other fillers are usually not beneficial. They may be deleterious.

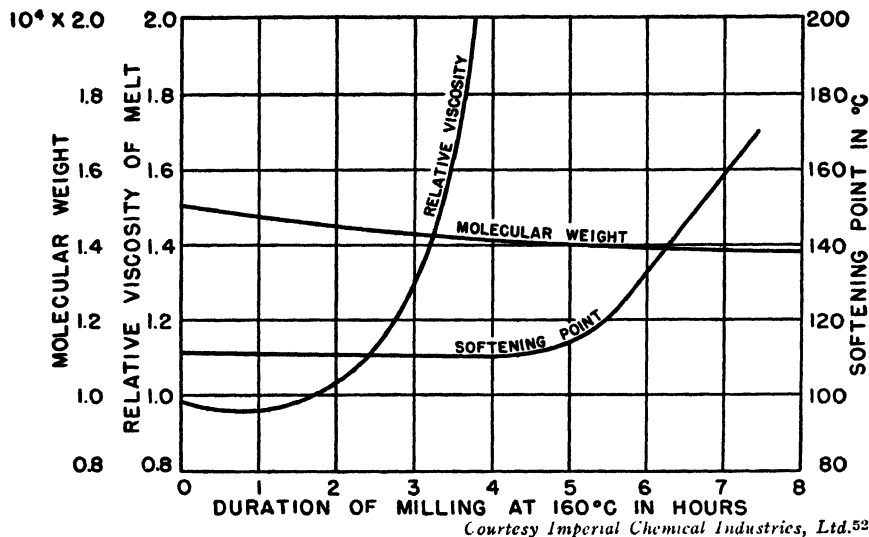


Figure 245. Progressive oxidation of Grade 20 "Alkathene" on open mills; effect on molecular weight, melt-viscosity, and softening point (ring and ball). Note that the molecular weights refer to the portion of material which is soluble in tetralin at 75°.

Polyethylene is insoluble in alcohols, esters, ether, glycerol, acetone, glacial acetic acid, carbon disulfide and linseed oil, regardless of temperature. It is relatively insoluble in other solvents at room temperature, but above about 70° it is dissolved by aromatic hydrocarbons such as xylene, toluene, and benzene. At elevated temperatures it also yields solutions with turpentine, mineral oils, carbon tetrachloride, trichloroethylene, and chlorobenzene. Its solubility characteristics are shown in Figures 243 and 244.

At 100°, polyethylene is not attacked by immersion in concentrated nitric or hydrochloric acids, nor by 50 per cent sodium hydroxide after 1 hour of exposure. It is slightly charred by concentrated sulfuric acid under these conditions. It is unaffected by ultraviolet light and by ozone at room temperature. In vacuum, decomposition begins to occur

at about 300°. In air, oxidation begins to be apparent at about 120° and proceeds fairly rapidly at 200°.

Oxidation is also brought about by milling on hot rolls. While the extent of this reaction is only slight, it is nevertheless sufficient to cause a marked change in several physical properties if it is sufficiently pro-

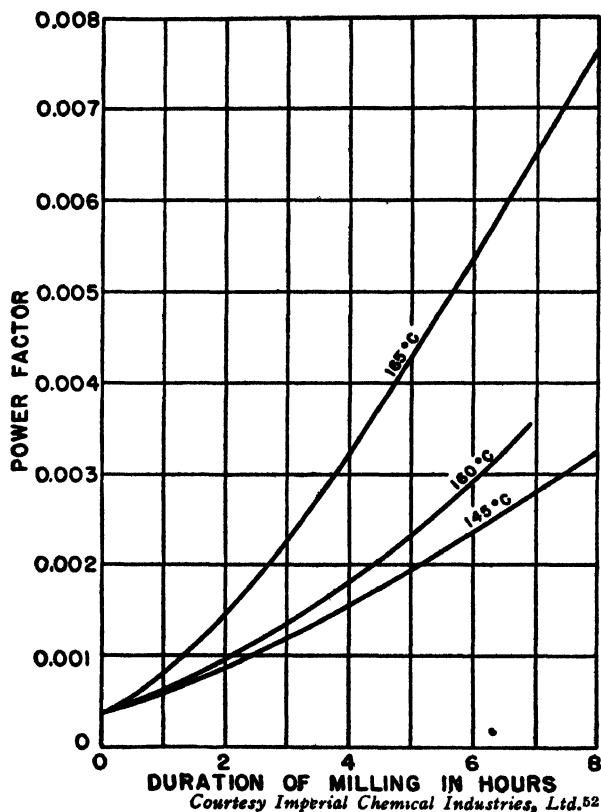


Figure 246. Increase in power factor of Grade 20 "Alkathene" caused by milling in air at different temperatures. Frequency of measurement: 1.6×10^7 cycles/sec.

longed. Alteration of dielectric characteristics is especially pronounced. Figures 245 to 247 illustrate this behavior.

Typical properties of polyethylene are listed in Table 123.

Fabrication. Polyethylene can be molded by extrusion, injection, or compression methods. It possesses a particularly high coefficient of thermal expansion which increases rapidly with temperature until the softening point is reached, where it drops and remains constant with further temperature rise. Its volume contraction in cooling from 120°

Table 123. Typical Properties of "Polythene"^a

(Data given herein represents standard commercial grades of material and standard methods of testing except where otherwise noted.)

Property	Test Result	Test Method
Specific gravity	0.92	D71-27
Tensile strength, psi		(1) D638-42T ⁽²⁾
at -70° F	5,000	
at 77° F	1,700	
at 170° F	700	
Elongation, per cent at 77° F	30-500	(1) D638-42T ⁽²⁾
Modulus of elasticity, 77° F psi	14,600	(1) D638-42T
Flexural strength, 77° F psi	1,700	D650-41T
Stiffness, 77° F	13,300	(1) D747-43T
Impact, Izod -70, 77, 170° F ft lb/in	(3)	D256-41T
Rockwell	13R	ARL. M-29
Flow temperature, ° C	104	D569-43
Deformation under load, 122° F per cent	20	(4) D621-43
Strain release temperature, ° C	75-80	ARL. M-15
Yield temperature, ° F	140	(1) ARL. M-8
Heat distortion temperature, low load, ° F	122	(5) D648-42T
Specific heat, cal/gm/° C	0.5	
Coefficient of expansion, per ° F	10.5×10^{-5}	D696-42T
Thermal conductivity, Btu/hr/ft ² /° F/in	2.96	D325-31T
Dielectric strength, step by step, V/M	1,000	(6)
Volume resistivity, ohm-cm	10^{17}	(6)
Water absorption, per cent	0.01	D570-42
Flammability, in/min	Ignites and burns slowly	
Outdoor exposure	No discoloration	(7)
Accelerated weathering	No discoloration	(7)
Methods of working	Inj., compr., extr., cal.	
Basic color	White translucent	
Resistant to	Water, alkalies, acids, and oxygenated solvents	
Not resistant to	Chlorinated solvents, aliphatic and aromatic hydrocarbons at elevated temperatures	
Outstanding for	Moisture resist., elect. prop., toughness, workability	
Major uses	Electrical insulation, tubes, containers	

⁽¹⁾ Average values reported. May vary considerably with method of specimen preparation (inj., comp., ext., etc.).

⁽²⁾ Tensile tests made at speed of 1 in/min.

⁽³⁾ Does not break at room temperature in 4 ft lb machine. 0.50 ft lb at -70° F.

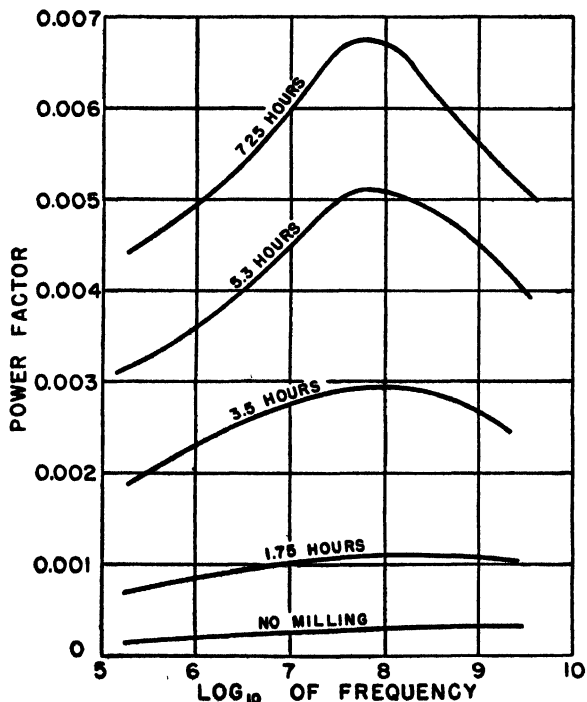
⁽⁴⁾ Tests run at a load of 1200 psi since the 4000 psi loading of the standard test was designed for more rigid plastics.

⁽⁵⁾ Maximum fiber stress 66 psi.

⁽⁶⁾ Values given are for early experimental "Polythene."

⁽⁷⁾ Tensile strength and elongation drop in absence of stabilizer.

to 20° is 12.5 per cent, more than half of which occurs between 120 and 80° during recrystallization. Because of these characteristics, slow cooling of extruded material is essential in order to prevent formation of voids. Likewise, slow cooling of compression molded articles, with con-



Courtesy Imperial Chemical Industries, Ltd.⁵²

Figure 247. Power factor of polyethylene and oxidized polyethylene. Variable frequency measurements at room temperature. Oxidation effected by milling at 160° for time specified on each curve.

tinued application of pressure until cold, is desirable to minimize internal strain.

For extrusion, both the cylinder and die temperatures should lie between 115 and 160°. Compression molding should be carried out within the same temperature range. Injection molding cylinder temperatures should lie between 175 and 260°.

Polyethylene articles can be machined, cut, blown, blanked, or swaged without difficulty.

Sheets of polyethylene can be fabricated by extrusion, calendering, or slicing.

Solutions of polyethylene can be prepared in hot xylene or other sol-

vents of the type listed above and are applicable in coating paper and cloth, as well as in adhesive formulation. Polyethylene may also be flame-sprayed by a modification of the Schori gun.

Spinning of high molecular weight grades of polyethylene and cold-stretching of the resulting fibers is expected to yield a new type of synthetic textile.

Applications. The principal application for polyethylene thus far has been in military electric insulation, especially radar, where advantage has been taken of its remarkable dielectric properties. Potential uses include bottle caps and liners, collapsible tubes, flexible pipe and tubing, water-proof sheeting and surface coatings, and such molded articles as battery parts and ice cube trays. Artificial silk is a potential outlet for this new plastic.

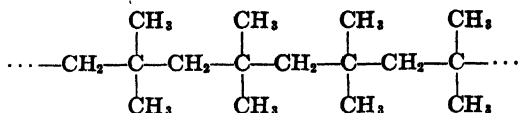
Polybutenes

The polymerization of isobutylene by means of sulfuric acid and other catalysts to low molecular weight liquid products is a reaction which has long been known and which has lately become of immense practical value in the manufacture of diisobutylene for conversion into isooctane. During the decade of the 'thirties it was found that at relatively low temperatures and in the presence of Friedel-Crafts type catalysts, notably boron trifluoride, isobutylene polymerizes to much higher molecular weight products ranging from viscous liquids to elastic solids, the highest members of the series being more rubber-like than rubber itself. The lower members, between 2000 and 10,000 molecular weight, were first developed in Germany by Otto and Mueller-Cunradi. Higher polymers were later produced as the result of joint research carried out by the Standard Oil Development Co. and the I. G. Commercial products were placed on the market in Germany under the name "Oppanol." They first appeared in this country about 1935 under the name "Viskanol" which was soon changed to "Vispronal" and then to "Vistanex." In Great Britain, polybutenes have been sold as "Isolene."

"Vistanex" has been made available in several grades: 7000, No. 6, Medium, and High Molecular Weight—the degree of polymerization increasing in the order named. The designations LM, MM and HM have also been used, corresponding to low (5,000–15,000), medium (30,000–150,000), and high (above 150,000) molecular weight. High molecular weight polybutene has also been marketed under the name "Synthetic 100."

Chemistry. Polybutenes can be synthesized in molecular weights ranging from 2000 to over 400,000. The commercial products are made essentially from isobutylene, but contain varying amounts of the normal

isomeric olefins. Disregarding the latter, a typical segment of a polybutene macromolecule is as follows:



The marked crystalline character of the x-ray diffraction pattern of stretched polybutene affords physical evidence of the regular symmetry of its molecule. Pyrolysis of 20,000 polymer at 350°, moreover, yields about 50 per cent of isobutylene and from 20 to 25 per cent of octenes,

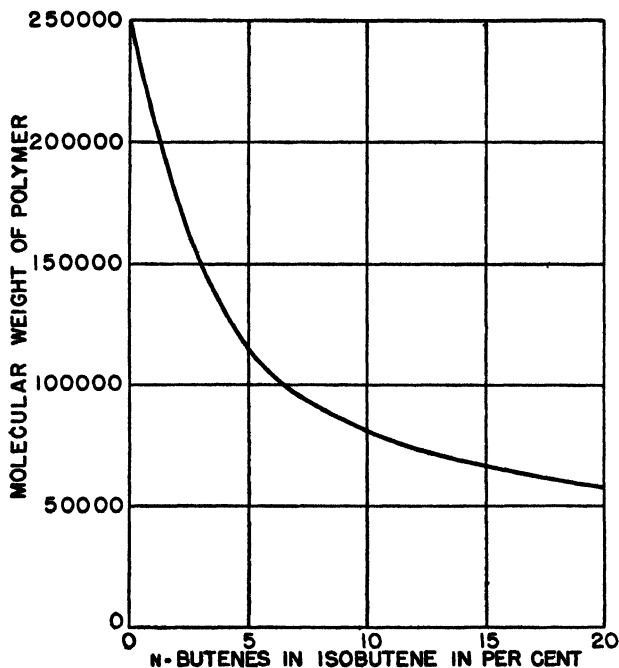


Figure 248. Effect of *n*-butenes on the molecular weight of polyisobutylene produced at -95° using boron trifluoride catalyst. (Thomas, Sparks, Frolich, Otto, and Mueller-Cunradi⁹³)

chiefly the diisobutylenes. Chemical evidence for the above formula is thus available, although the appearance of some octenes in the products of decomposition, other than the dimers of isobutylene, suggests the possible presence of a small amount of material less symmetrical in structure than that shown above.

The formation of polyisobutylene is an extremely rapid reaction which occurs almost explosively at sub-zero temperatures. Under properly

controlled conditions, 90 per cent yields, or better, of this elastolene can be obtained in a fraction of a second from liquid isobutylene. The rate of polymerization does not decrease perceptibly as the temperature is lowered.

Boron trifluoride is an extremely effective catalyst for the reaction and is preferred industrially. Aluminum chloride and titanium tetrachloride are also efficacious. Hydrogen sulfide, mercaptans, anhydrous hydro-

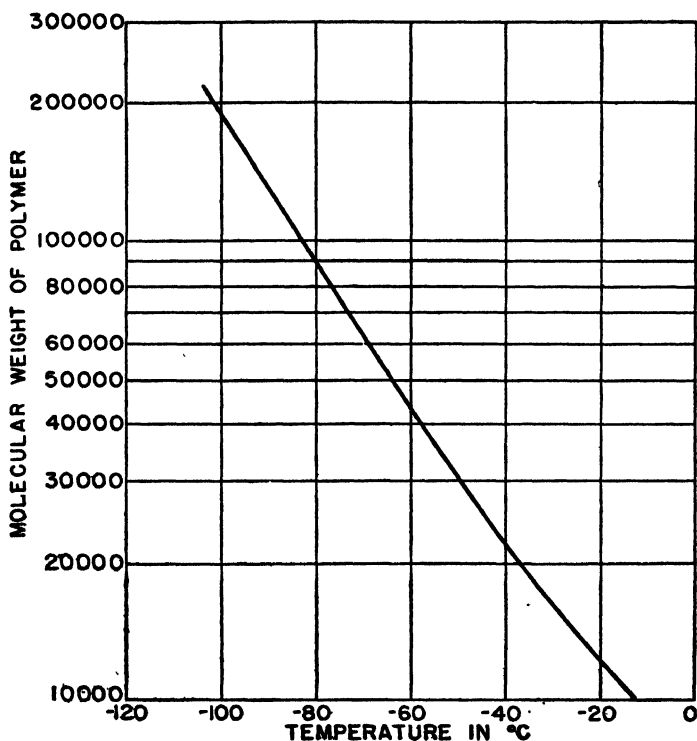


Figure 249. General effect of reaction temperature on the molecular weight of polymers produced from isobutene. (Thomas, Sparks, Frolich, Otto, and Mueller-Cunradi⁹³)

gen fluoride, and anhydrous hydrogen chloride act as poisons, the last two depressing the molecular weight of the polymer.

The nature of the product is subject to variation by control of the purity of the raw material, the temperature of reaction, and the use of diluent.

The presence of other olefins in the isobutylene employed may markedly affect the molecular weight of the polymer. Ethylene and propylene are without effect, but the normal butenes decrease polymer size, as shown by Figure 248.

Small amounts of dimers and trimers of isobutylene lower both the yield and molecular weight of the polymer. This observation is of special theoretical significance because it affords striking proof that the formation of long elastolene chains does not pass through the conventional dimeric and trimeric stages.

Various chemicals present to the extent of 0.5 per cent are capable of accelerating polymerization and increasing the size of the polymer. Such

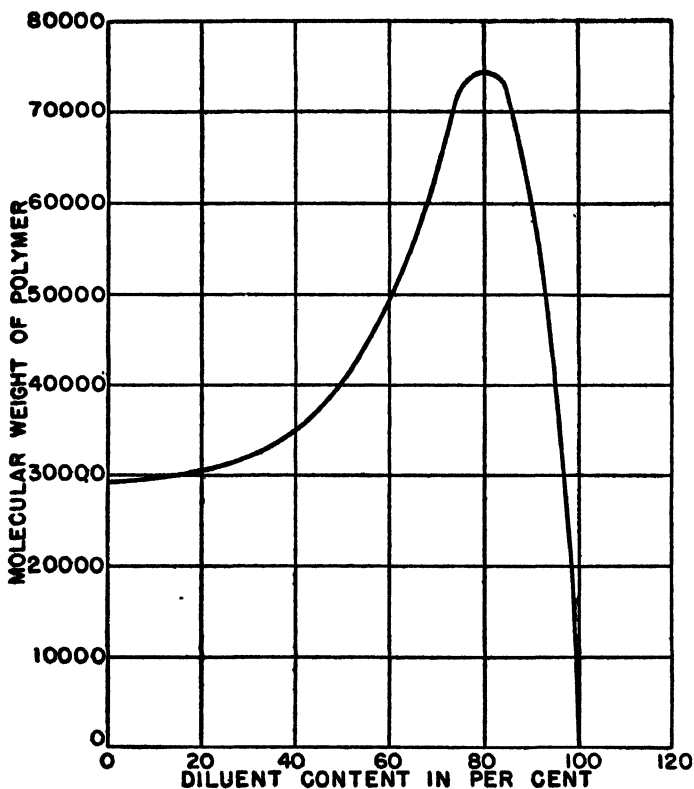


Figure 250. General effect of diluent concentration on the molecular weight of polymers produced from isobutene at -78° . (Thomas, Sparks, Otto, Frolich, and Mueller-Cunradi⁹³)

compounds include certain phenols, formaldehyde, and sulfuric and nitric acids.

As the temperature of polymerization decreases, the molecular weight increases rapidly as shown by Figure 249.

The use of diluents facilitates temperature control by moderating the violence of the reaction. Probably because of this fact the molecular weight of the polymer increases exponentially up to a limiting concen-

tration of about 80 per cent by volume of diluent (at -78°). Beyond this point the customary effect of dilution on polymerization reactions appears to predominate suddenly and the molecular weight of the polymer drops off abruptly, as shown by Figure 250.

The Staudinger viscosity constant for use in calculating the molecular weight of polybutenes is 0.77×10^{-4} .

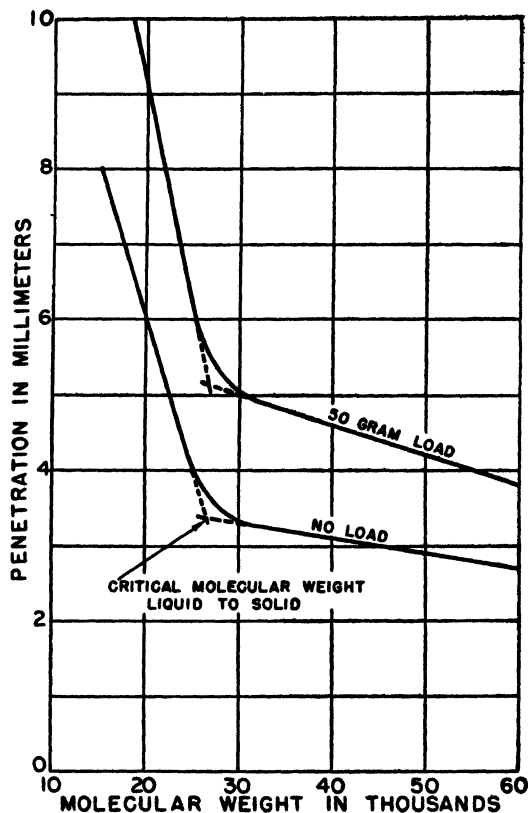


Figure 251. Penetration-molecular weight relation for polybutenes at 25° by the ASTM method for wax and asphalts. (Thomas, Zimmer, Turner, Rosen, and Frolich⁹⁴)

Properties. The polybutenes are available in a considerable range of properties. The lower polymers are clear, viscous, very sticky syrups which flow with increasing difficulty as the molecular weight rises. The higher members of the series are colorless rubber-like solids whose toughness and strength increase with molecular weight. Penetration data indicate that there is a critical point at which these polymers change from viscous fluids to elastic solids in the neighborhood of a molecular weight of 27,000. This fact is illustrated in Figure 251.

Below 80,000, these polymers possess very little strength. At about this point they begin to acquire tensile strength which increases gradu-

ally until at 150,000 it is in the order of 500 lbs per sq in. Depending on its mechanical treatment before testing, the tensile strength of 200,000 polybutene may be as much as 1900 lbs per sq in.

Polybutenes of high molecular weight are subject to depolymerization by both mechanical and thermal means. Mechanical breakdown occurs by agitation in solution or by milling. Vigorous agitation of 275,000 polybutene in *n*-heptane (1 mg per cc) during two hours, for example, has been shown to result in a decrease of molecular weight to 150,000.

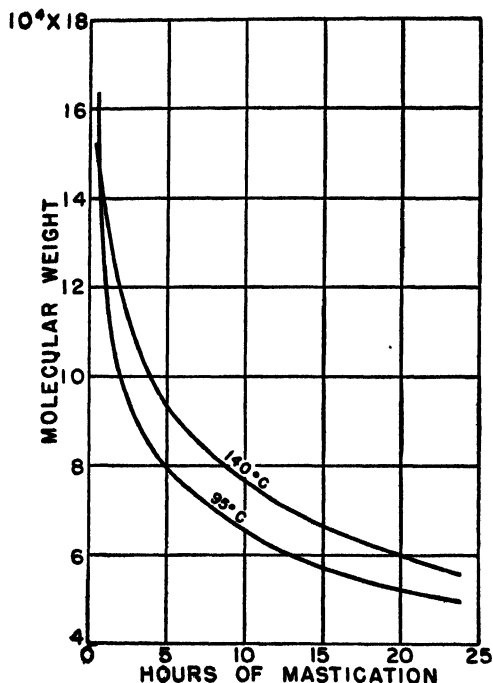


Figure 252. Molecular weight degradation of polyisobutene vs. time of Banbury mastication. (Sparks, Lightbown, Turner, Frolich, and Klebsattel⁸³)

The effect of time and temperature of Banbury milling is shown in Figure 252. The results are similar, but not as rapid as those obtained with natural rubber.

Thermal degradation occurs at temperatures above 100°. After two hours of heating 140,000 polybutene at 150°, for example, its molecular weight decreases to 30,000–40,000. Stabilizers are known which greatly retard both mechanical and thermal breakdown.

Regardless of molecular weight, all of the polybutenes show both cold flow and tack although these two properties become less conspicuous with increasing molecular weight.

The polybutenes possess unusual reversible extensibility and high elongation. Unfilled, they can be stretched without breaking to as much

as 1000 per cent or more. The incorporation of fillers decreases stretch, but polybutenes take up these materials with avidity on the rubber mill. It is possible to incorporate 1000 per cent of carbon black in high molecular weight "Vistanex," for example, without loss of elastic properties. Fillers do not exhibit any reinforcing action on the physical properties of the polybutenes. Strength is sacrificed to some extent by their use. Tack and cold flow are somewhat reduced.

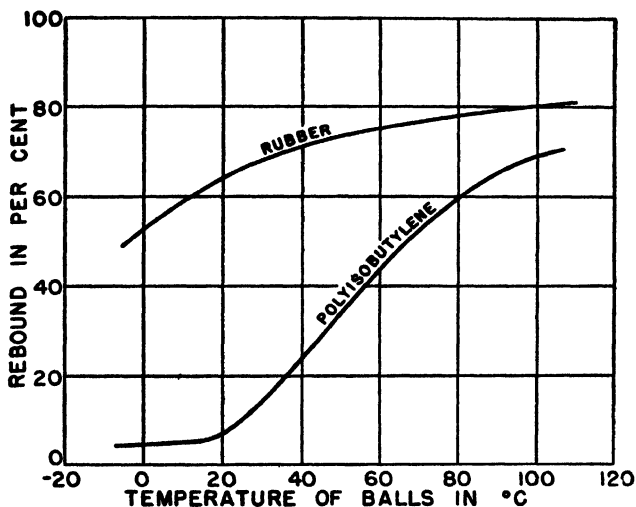


Figure 253. Rebound of 168,000 molecular weight polyisobutene balls and vulcanized pure gum rubber balls falling under their own weight from a height of 1 meter. (Sparks, Lightbown, Turner, Frolich, and Klebsattel⁸³)

The polybutenes are not brittle at -78° . They possess an unusually wide range of flexibility, failing to liquefy at 180° , despite some thermal breakdown. For this reason they were once recommended as additives for flattening the viscosity index of lubricating oils and greases.

The rebound or bounce of the polybutenes is dependent on temperature. Unlike many other elastomers they exhibit almost no rebound at room temperature, but approach natural rubber in this respect at 100° (see Figure 253).

The higher polybutenes possess excessive elastic memory or nerve at ordinary temperatures. It can be decreased by heating to about 100° . Compounding with fillers or miscible oils and waxes reduces nerve, but only at a sacrifice of other physical properties.

As would be expected from the saturated nature of these polymers, they cannot be vulcanized by means of sulfur. They can, however, be mechanically combined with other vulcanizable elastomers. In such

combinations the physical properties of the polybutenes become paramount where they are present in excess of 50 per cent.

The saturated character of the polybutenes is further reflected in their resistance to oxygen and ozone. They can therefore be combined with natural rubber to improve the aging characteristics of the latter. They are likewise resistant to concentrated acids and alkalis, although they are attacked by nitric and sulfuric acids at elevated temperatures and by the former even on prolonged standing at room temperature. They show the typical resistance of saturated hydrocarbons to other reagents. Towards hydrogen fluoride they are inert, but they are slowly hardened by chlorine and bromine. Direct sunlight and ultraviolet cause gradual depolymerization, especially in the case of the higher polymers.

The polybutenes dissolve in aliphatic hydrocarbons at room temperature. Aromatic hydrocarbons dissolve all but the highest molecular weight products. Certain chlorinated solvents dissolve them; oxygenated solvents in general do not. They are compatible with paraffin wax, hydrogenated coumarone-indene resins, rosin, ester gum, montan wax, and "Petrex" 5 and 21, but are incompatible with most other resins and with animal and vegetable fats, oils, and greases.

The density of the polybutenes is about 0.9, varying slightly with molecular weight. Some of their electrical properties are shown in Table 124.

Table 124. Electrical Properties of Polybutenes ⁷⁸

Temperature (° C)	Power Factor (800 cycles)	Dielectric Constant (800 cycles)	Resistivity (ohm-cm)	Breakdown Voltage (kv/mm)
20	0.0004	2.3	> 10 ¹⁵	23
85	0.0005	2.2	> 10 ¹⁵	23
Frequency in Cycles		Power Factor (20° C)		
800		0.0004		
1.2 × 10 ⁶		0.0011		
2.8 × 10 ⁶		0.0012		
6.7 × 10 ⁶		0.0015		

Because of their hydrocarbon character, the polybutenes possess exceptionally good resistance to water and water vapor.

Uses. The polybutenes have found especial utility in combination with natural rubber for cable sheathing applications. The resistance of rubber toward ozone, acids, and water is thereby greatly enhanced. Steam hose, belt coverings, inner tubes, gas masks, and balloon cloth are other recommended applications for rubber-polybutene mixtures.

Polybutenes alone have found extensive use as the gasoline-soluble liner for aircraft bullet-proof gas tanks.

They are used in conjunction with fillers in numerous gaskets, packing and caulking compounds.

They have found utility as plasticizers for various waxes and resins. Blends of less than five per cent with paraffin wax improve low temperature flexibility of waxed sheets. Above this concentration, however, blocking may be encountered. Paraffin wax blends have been especially useful in packaging frozen foods. Their utility in conjunction with polyethylene has been mentioned in the preceding section.

Admixed with various asphalts and pitches they often improve low temperature flexibility, increase softening point, and enhance adhesion so that such mixtures have found use, for example, in improved coatings for refinery pipe linings and sealing compositions. The compatibility of polybutenes with carbonaceous pitches usually decreases with increasing molecular weight.

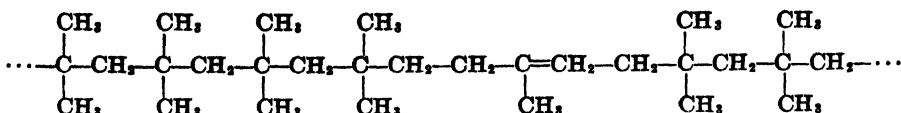
Polybutenes are employed in such miscellaneous applications as sealing compositions and pressure sensitive adhesives for use on cellophane, masking, and surgical tapes. Fluid types have found limited use as a replacement for oil in high-voltage paper cable.

They have been used to flatten the viscosity index of lubricating oils and to improve stringiness of greases and special lubricants. Unfortunately, their service performance in lubricating oils does not appear to have lived up to early predictions based on relatively simple laboratory tests. They are available as lubricant additives in mineral oil solution under the trade name "Paraflow" and as grease components under the designations "Paratone" and "Paratac."

"Butyl" Rubber

Closely allied to the polybutenes is "Butyl" rubber. This material, or rather these materials—for a whole series of copolymers is included generically under the trade name "Butyl"—have been developed by the Standard Oil Company of New Jersey.

Chemistry. "Butyl" is a cross between the polybutenes and the polybutadienes. Like the former, it is prepared by low temperature polymerization using Friedel-Crafts type catalysts. Mixtures of olefins and diolefins are employed, the products being linear copolymers possessing a relatively low degree of unsaturation. In present industrial practice, isobutylene is the olefinic constituent and isoprene the diolefin. A code letter following the word "Butyl" indicates the specific diolefin used. A portion of the molecular structure of "Butyl" may be represented as follows:



Only a few per cent of diolefin is employed. Commercial "Butyl" possesses from 1 to 3 per cent as much unsaturation as natural rubber. The exact amount in any particular copolymer is indicated by the figure following the lettered grade, for example: "Butyl" B-1.45 or "Butyl" B-3. By introducing only a slight degree of unsaturation into an otherwise paraffinic chain an elastomer results which possesses enough double bonds to allow vulcanization with sulfur to yield a product closely resembling soft rubber in physical characteristics, but very nearly saturated. The reactivity of natural rubber, attributable to its highly unsaturated character, is thus eliminated in "Butyl" and the vulcanized product is relatively very stable to oxygen, ozone, strong acids, and even copper, cobalt and manganese compounds which cause serious deterioration of natural rubber goods.

As the proportion of diolefin used during polymerization is increased, the unsaturation of the product rises correspondingly. Tensile strength and elongation decrease, but heat stability and hysteresis properties, as reflected especially in heat build-up, improve rapidly. Curing time is shortened.

Quinone dioxime can be used advantageously with "Butyl" as a vulcanizing agent.

Although commercial "Butyl" is reported to possess a molecular weight in the range of 40,000 to 80,000, copolymers as high as 400,000 can be prepared. Depending to some extent on composition, increasing molecular weight results in higher moduli, better rebound and heat build-up characteristics, and increased heat stability of the cured product. Plasticity of the uncured product, and therefore processability, suffer.

Properties. "Butyl" is odorless and tasteless. It possesses a density of 0.91. Uncured, it resembles the polybutenes and has a consistency comparable to that of well masticated natural rubber. It is tacky and undergoes cold flow. Like the polybutenes, it does not bounce appreciably at room temperature and this curious lack of rebound carries over to the vulcanized product, although at 100° it approaches natural rubber in this respect. Compounding with small amounts of elasticators improves rebound as well as heat build-up and processability. Aromatic ethers like trichlorodiphenyl ether ("Dow 3X"), benzyl ether, and ethyl diphenyl ether, certain aromatic hydrocarbons such as *p*-cymene, and chlorinated biphenyls ("Aroclors") are useful elasticators.

Uncured "Butyl" is supplied to the trade admixed with one part of zinc stearate and one-half part of phenyl- β -naphthylamine. It differs from natural rubber in that no breakdown is required on the mill before compounding. On cold rolls it is tough and ropy. Between 80° and 100°

it becomes soft and smooth, but on heating at higher temperatures, it acquires a crumbly character. In the activity of vulcanization accelerators and in the effect of fillers "Butyl" also differs from natural rubber. Moreover, unsaturated softeners and elastoprenes cannot be used in conjunction with "Butyl" because of their preferential reaction with sulfur.

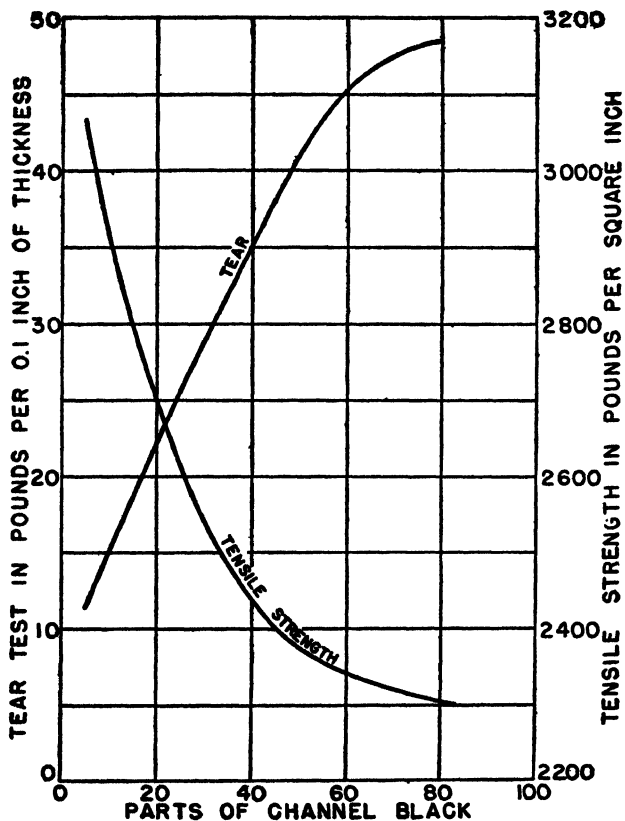


Figure 254. Relation between tensile strength, tear resistance (Crescent), and channel black ("Kosmobile 66") content of vulcanized "Butyl A." (Thomas, Lightbown, Sparks, Frolich, and Murphree⁹²)

"Butyl" can be cured with the assistance of ultra accelerators of the thiuram type, such as tetramethylthiuram mono- and disulfides, zinc butyldithiocarbamate, and dipentamethylenethiuramdisulfide, preferably in combination with mercaptobenzothiazole or an analogous compound which aids in decreasing heat build-up and hot flow. Most other rubber accelerators, however, yield poor vulcanizates with "Butyl."

Carbon black does not exercise reinforcing action on the tensile strength of this elastolene, nor do other fillers. On the contrary, both tensile and elongation usually decrease gradually with such additions. Tear resistance and modulus, however, are improved, especially by semi-reinforcing furnace blacks, as illustrated by Figure 254. Resistance to abrasion, cutting, and shock, as well as toughness, are also improved by addition of suitable fillers.

"Butyl" is vulcanized at temperatures between 140° and 200°. It is slower curing than natural rubber, but is not easily overcured. Indeed, its hysteresis properties improve progressively with increase of curing time. The relation of tensile strength and elongation to curing time is shown in Table 125.

Table 125. Effect of Temperature on Curing Rate of Butyl Rubber ⁹²

Cure (min)	138° Cure		145° Cure		150° Cure		155° Cure	
	Tensile Strength (lb/sq in)	Elongation (%)	Tensile Strength (lb/sq in)	Elongation (%)	Tensile Strength (lb/sq in)	Elongation (%)	Tensile Strength (lb/sq in)	Elongation (%)
15	Undercured	—	1300	1270	2400	1130	2780	1070
30	1400	1260	1970	1080	3350	1090	3540	1000
60	2720	1180	2640	1000	3360	970	3510	980
120	2930	1030	3360	980	3620	980	3640	970

Cured "Butyl" in general is similar to soft rubber insofar as elasticity and strength are concerned. Its stress-strain curve, however, differs in shape from that of natural rubber, for relatively little stress is required to produce elongations of 500 to 700 per cent. Beyond this point, the curve resembles that of natural rubber, as shown by Figure 255.

"Butyl" is not ranked among the solvent resistant synthetic rubbers for it is attacked by aliphatic hydrocarbons. Oddly enough, it is somewhat resistant to aromatics like benzene and toluene, as well as to ethylene dichloride and various oxygenated solvents. Although swelled about 100 per cent on prolonged immersion in oleic acid, it is much more resistant to vegetable and animal fats and oils than is natural rubber.

"Butyl" is far superior to natural rubber in resistance to oxygen, ozone, and most chemical reagents.

Although resistant to hydrochloric and sulfuric acids, "Butyl" becomes spongy on exposure to concentrated nitric acid and, at 100°, it undergoes marked loss of strength therein.

"Butyl" possesses better flex resistance than natural rubber and retains elastic qualities at temperatures as low as - 80°. Although more stable in sunlight than natural rubber, it does tend to depolymerize slightly. This behavior can be overcome by loading with 30 per cent or more of carbon black. In comparison with natural rubber it is also relatively heat-stable, as shown by Table 126.

The water-resistance and permeability of "Butyl" to various gases is excellent, the latter being illustrated by Table 127.

"Butyl" possesses valuable electrical properties listed in Table 128 which compares the properties of pure gum natural rubber with those of pure gum "Butyl."

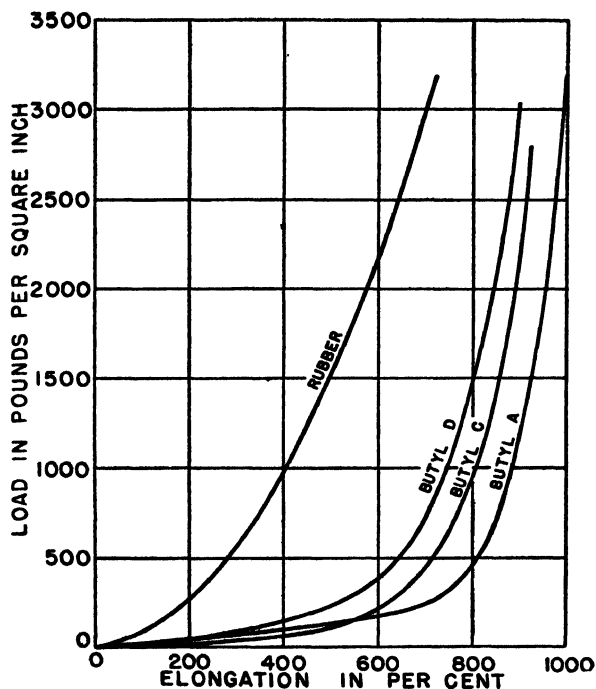


Figure 255. Stress-strain characteristics of three types of "Butyl" as compared with natural rubber. (Thomas, Lightbown, Sparks, Frolich, and Murphree⁹²)

Applications. "Butyl" has been recommended for use in fire and air hose, tank linings, conveyor belts, molded goods, electrical insulation, foodstuffs tubing, balloon fabric, gas masks, pontoons, and naval matting. Properties making it particularly well suited for such applications are resistance to age, light, water, and chemicals, electrical insulating characteristics, and impermeability to gases. The last-named property adapts "Butyl" to use in fabrication of inner tubes for tires which are not subjected to heavy duty sufficient to cause hot flow. "Butyl" can be used in automobile tires, but not advisedly. It was originally planned to manufacture 182,000 long tons of this elastomer per year to relieve the rubber shortage. Much of this amount would have gone into tires. In this application, however, "Butyl" is admittedly as yet only a poor

Table 126. Heat and Age Stability of Rubber and "Butyl" Rubber in Geer Oven ⁸²

Loading (on Total Gum)	Original	Tensile Strength (lb/sq in)		24 hr, 150° oven
		14 days, 70° oven	7 days, 100° oven	
Natural Rubber				
No. 1 pure gum	3400	2500	0 (brittle)	Melt
No. 2 pure gum (heat-resistant)	2700	2780	0 (brittle)	Melt
"Butyl" Rubber				
Pure gum	3500	3500	2870	Melt
85% Calcene	2300	2320	1800	Melt
50% Gastex	2600	2300	2300	660
85% Gastex	2000	1800	1800	670
50% gas black *	3300	3000	2720	920
85% gas black *	2600	2260	2180	1330
50% zinc oxide	3340	2850	2040	Melt
85% zinc oxide	3100	3000	2350	Melt
50% P-33	3000	2560	2000	440
85% P-33	2300	2000	1870	620
50% lithopone	3300	3150	2300	Melt
85% lithopone	3000	2560	1870	Melt

* Cabot No. 9 gas black

Table 127. Approximate Relative Gas Permeabilities through Pure Gum Stocks ⁸²

Gas	Ratio of Rate of Diffusion through Natural Rubber to Rate of Diffusion through "Butyl" Rubber
Hydrogen	10-12.5
Helium	6 or greater
Nitrogen	10-20
Sulfur dioxide	Very great

Table 128. Electrical Properties of "Butyl" and Natural Rubbers,
Measured at 1000 Cycles ⁸²

	"Butyl" Rubber		Natural Rubber	
	0.6		0.5	
Dielectric strength, kv/mil	Dry	Wet*	Dry	Wet*
Dielectric constant (1000 cycles)	2.11	2.10	2.46	2.76
Power factor, %	0.04	0.05	0.04	0.16

* 88 hours in distilled water; surface wiped dry for measurement.

substitute for rubber. Tire life is about 20,000 miles at speeds of 40 miles per hour or less.

The solubility of "Butyl" in paraffinic hydrocarbons adapts it especially well for use in cements and coating compositions because toxic aromatic hydrocarbon solvents normally employed for these purposes with natural rubber can be avoided.

"Butyl" has been manufactured as part of the Government rubber program under the designation GR-I (Government Rubber—Isobutylene). The production originally planned was cut back to 75,000 long tons, manufacture of which was to be distributed as follows:

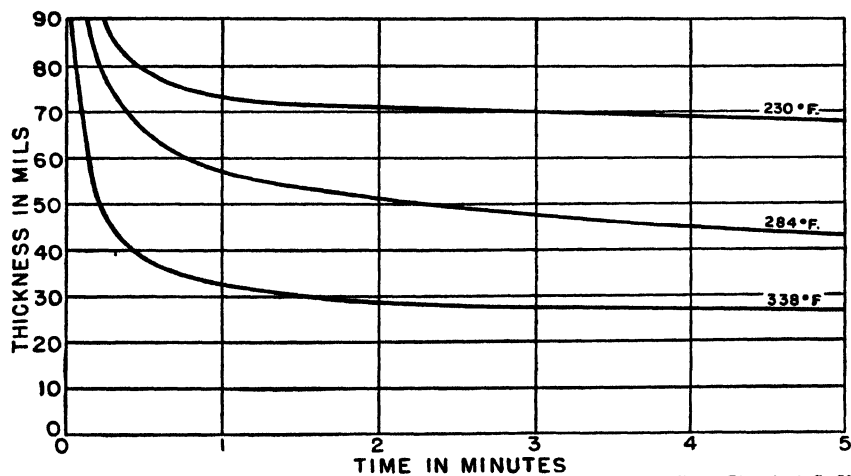
Polymer Corp., Ltd., Sarnia, Ont.	7,000 long tons
Standard Oil Co. of La., Baton Rouge, La.	38,000 " "
Humble Oil & Refining Co., Baytown, Texas	30,000 " "

Actual 1944 production, however, was only 48,513,000 pounds.

"Flexon," dubbed "bath-tub Butyl," was the name applied to "Butyl" rubber which was to be produced by small refiners on their premises in simple equipment and in small batches, using solid carbon dioxide added directly to the reacting mixture as a coolant. Obvious difficulties in lack of uniformity, poor physical properties resulting from improper control of reaction, excessive waste of isobutylene through high volatilization losses, and insufficient supplies of dry ice led to abandonment of the projected manufacture of this product.

Styrene Copolymer Elastolenes

A new-comer to the field of elastolenes is "Styraloy," manufactured by the Dow Chemical Company and available in two grades of molding powder designated as 22 and 22A. Relatively little information has yet



Courtesy The Dow Chemical Co.⁸⁰

Figure 256. Flat plate flow properties of "Styraloy 22." (Original sample height: 0.125 inch. Load: 237 lbs/sq inch. Upper flat plate diameter: 2 inches.)

been released concerning this material, but it appears to be a copolymer of styrene and butadiene in which styrene is the major constituent. It possesses an iodine number of about 5.3 and it tends to undergo some self-vulcanization on prolonged heating. It is substantially hydrocarbon in character, but contains a small quantity of added antioxidant.

"Styraloy" has been developed primarily for use in electric cable, especially ignition and low frequency coaxial cable where low tempera-

ture flexibility and minimum cold flow at elevated temperatures are required of one material, as in aviation applications.

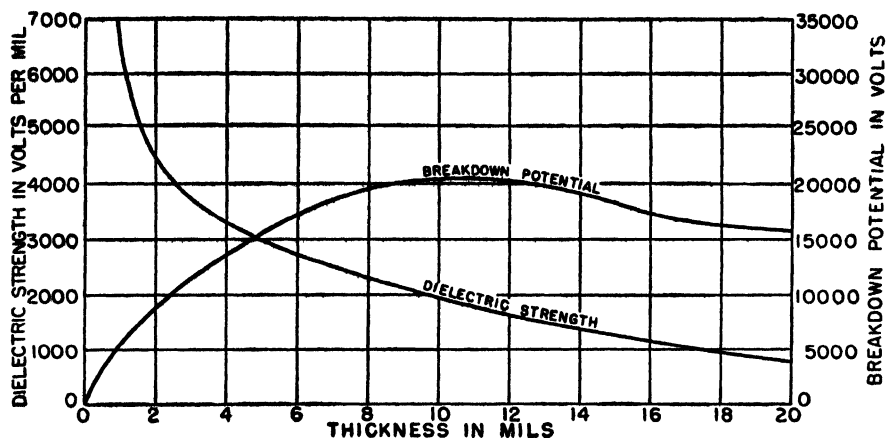
"Styraloy" is dark slate gray in color. Its density is 0.96. It is flexible at temperatures as low as -70° , although it is more stiff and less resilient than most grades of soft rubber. Its extensibility varies from about 200 per cent for compression molded and extruded material to only 16-20 per cent in the case of injection molded articles. Elongation is only partially reversible for considerable cold flow occurs during stretching. Flat plate flow of "Styraloy" is shown in Figure 256.

Current grades of "Styraloy" appear to be well adapted to compression molding and extrusion. With reasonable care they can also be injection molded. It is important to avoid excessive heating of the material. If desired, "Styraloy" can be drawn after extruding, although in some cases it may be advisable to cool the extruded material to $200-250^{\circ}$ F before drawing. Plasticization also aids drawing operations.

General physical properties of "Styraloy" are listed in Table 129.

Table 129. Physical Properties of "Styraloy" 22³⁰

Tensile strength	1000-1200 lbs/sq in
Elongation at break	200-250% (compression molded or extruded) 16-20% (injection molded)
Weld strength (injection molded)	500 lbs/sq in
Impact strength	1.2-1.8 ft lbs/in of notch
Distortion under heat, A.S.T.M.	62-65°
Molding conditions	
Extrusion	Feed zone—unheated, below 300° F Barrel and cross head— $340-350^{\circ}$ F Die— $350-370^{\circ}$ F
Compression molding	Temperature— $120-150^{\circ}$
Injection molding	Pressure—500-1000 lbs/sq in Temperature— $420-480^{\circ}$ F Pressure—5000-10,000 lbs/sq in
Bulking factor	2-2.5
Density (25°)	0.957
Heat conductivity	4.32×10^{-4} cal/sec/° C/cm/cm ²
Specific heat at 30°	0.405 cal/gm/° C
Linear coefficient of thermal expansion	
- 20 to $+84^{\circ}$	1.79×10^{-4} cm/cm/° C
+ 84 to $+110^{\circ}$	2.26×10^{-4} cm/cm/° C
Burning rate, A.S.T.M.	1 in/min
Water absorption, A.S.T.M.	
24 hrs	0.2%
48 hrs	0.3%
Water vapor transmissivity (25°)	
5.0 mils thickness	88.1 gm/sq m/24 hrs
Abrasion resistance	Comparable to natural rubber
Flex resistance, 1 kg load, 180° bend	Up to 50,000 bends, depending upon method of fabrication
Tear resistance, A.S.T.M.	240 lbs/in
Machinability	Feasible



Courtesy The Dow Chemical Co.³⁰

Figure 257. Dielectric characteristics of "Styraloy 22" versus thickness.

"Styraloy" is relatively resistant to oxygen and ozone by comparison with natural rubber. Its corona resistance is far superior to that of rubber. Electrical properties are shown in Table 130 and Figure 257.

Table 130. Electrical Properties of "Styraloy" 22 at Room Temperature³⁰
(flat plate moldings, approx. 0.1 inch thick)

Dielectric Constant	1000 cycles	2.5-2.6
	1 megacycle	2.6-2.7
	50 megacycles	2.5
Power Factor, %	1000 cycles	0.07-0.12
	1 megacycle	0.05-0.10
	50 megacycles	0.35-0.40
	100 megacycles	0.40-0.50
Volume Resistivity	10 ³⁰ ohm-cm	
Dielectric Strength	3000 volts per mil at 5 mils	
	800 volts per mil at 20 mils	
	(also see Figure 257)	

Molded or extruded "Styraloy" will withstand ten hours' heating at 150° and 80 pounds air pressure without enbrittlement, but will discolor under these conditions. Continued exposure then produces progressive stiffening which will finally result in a brittle material. This change is probably caused by oxidation. In general, heat treatment reduces thermoplasticity, increases solvent resistance, and reduces conductor migration.

Like natural rubber, "Styraloy" is attacked by common solvents, but to a lesser degree.

It is compatible with many plasticizers such as dibutyl sebacate, tricresyl phosphate, and "Santicizer" 9. It is also compatible with many

synthetic and natural polymers such as polybutene, GR-S, "Hycar," "Thiokol" Type FA, neoprene, and natural rubber. If desired, small amounts of fillers, such as clays, carbon black, and wood flour can be mixed into "Styraloy," but in general it is not desirable to use large amounts of these materials unless it is in combination with other polymers which are themselves capable of assimilating the fillers.

In carload lots, "Styraloy" was priced in 1944 at 60 cents per pound.

"Pliolite" S-3, a new styrene-butadiene copolymer containing 15 per cent diolefin, appears to stand in an intermediate position between elastoprenes and elastolenes. It has been discussed in Chapter 16.

Elastothiomers

The elastothiomers constitute a group of elastomers quite unlike addition polymers and copolymers of unsaturated hydrocarbons heretofore discussed in this chapter, for they are double decomposition products of various dihalides and alkali polysulfides.

Although occasional references to a few aliphatic sulfur compounds of this nature occurred in the early scientific literature, such substances attracted little attention because of their uninviting amorphous character. In 1920, J. C. Patrick reacted ethylene dichloride with sodium polysulfide while seeking a new antifreeze. The product turned out to be a solid, more or less rubbery material, highly insoluble in most organic solvents. It later aroused the interest of Bevis Longstreth, then president of the Bevis Rock Salt Company for whom Patrick had been investigating new uses for salt. Longstreth organized the Thiokol Corporation in Kansas City, subsequently moving to New Jersey, and in 1930 "Thiokol" was first offered to industry, two tons being produced that year. Despite certain drawbacks—especially odor, it rapidly grew in favor because of outstanding oil resistance.

In 1938, the Dow Chemical Company undertook manufacture of this elastomer for the Thiokol Corporation. A few years later the latter company opened a "Thiokol" latex plant at Trenton, while Naugatuck Chemical, Ltd., of Canada now manufactures "Thiokol" stocks under license.

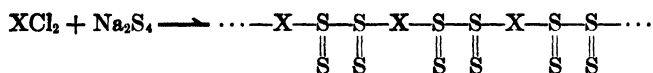
The position of "Thiokol" in the domestic rubber program has been rather uncertain. The Baruch Committee's recommendations originally called for production of 60,000 long tons per year to be used largely in recapping civilian tires. Admittedly a poor substitute in this application, it was believed that this easy-to-make elastomer would tide the nation over a difficult period despite its shortcomings. Fabrication problems, however, proved to be more serious than had been supposed; the odor even of the best grades was an insurmountable obstacle to

general use and production was cut back to 24,000 tons per year or less.

At about the same time that Patrick was carrying out his early work, J. Baer developed similar elastothiomers in Switzerland which were later commercialized by the German I.G. Polysulfide rubbers are now manufactured in several other countries, the most important being England, Russia, and Japan.

Chemistry

The fundamental reaction involved in the manufacture of elastothiomers is one of double decomposition between aliphatic dihalides and sodium polysulfide or other metal polysulfides. Long chains are formed, believed to have the following structure:



Reaction is carried out by slowly adding the dihalide, with vigorous agitation, to an aqueous solution of sodium polysulfide prepared from caustic soda and sulfur. The gravity of the polysulfide solution is adjusted to about the same density as the halide and a dispersing agent is preferably employed to facilitate reaction and, in case a latex is desired as the final product, to assist dispersion. Peptized starch and proteins have been suggested as suitable dispersing agents, but the most satisfactory material appears to be magnesium hydroxide used to the extent of 0.5–1 per cent of the water present. A water miscible alcohol may also be added to aid intimate contact of the reactants.

In carrying out this condensation, excess sodium polysulfide is employed for two reasons: first, for purposes of economy; second, because a rubber-like polymer is obtained if it exceeds the stoichiometric equivalent of dihalide whereas a viscous liquid results where the latter is in excess.

The reaction between aliphatic dihalides and sodium polysulfide is exothermic. Proper temperature control must be maintained either by cooling or by regulating the rate of addition of dihalide. Although reaction occurs at room temperature, it is best carried out around 70° under a reflux or in an autoclave. Depending on conditions, condensation may require from two to six hours.

On completion of reaction, the suspension is allowed to settle, decanted, and washed free from excess of sodium polysulfide and sodium chloride formed as a by-product. The elastothiomers are then coagulated with hydrochloric acid. Before precipitation, the polytetrasulfide may be treated further with caustic soda, as by heating at 80° for one hour. This operation eliminates the side sulfurs, thus yielding a polydisulfide,

. . . —X—S—S—X—S—S—X—S—S—X—S—S— . . . The reverse reaction, that is addition of sulfur to the polydisulfide, can be brought about by heating with elemental sulfur for 24 hours. After such treatment, no free sulfur can be extracted from the product by acetone, nor does sublimation change its empirical formula.

The physical properties of the thioplasts depend on the nature of X and on the amount of sulfur present in the monomeric unit. Some polymers are rubber-like, others are amorphous powders—plastic, but non-rubbery. Where four sulfur atoms are present in the monomeric unit, all reported polymers are rubber-like, regardless of the nature of X. Where only two sulfur atoms are present, four or more carbon atoms (or their equivalent such as oxygen) must be present in the monomeric unit in order to yield a polymer possessing rubber-like characteristics. Where only a single sulfur atom is present in the monomeric unit, the product is an amorphous powder even where X contains a total of six carbons and two oxygens. In the case of ethylene polysulfide, rubbery properties begin to appear where an average of 2.5 sulfur atoms per monomeric unit is attained, corresponding to one coordinately combined sulfur atom for every other monomeric unit:

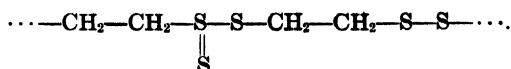


Table 131 emphasizes these relationships.

Principal halides used in production of domestic elastothiomers are ethylene dichloride, β,β' -dichlorodiethyl ether, and dichloroethyl formal. Propylene dichloride is less satisfactory. In certain grades of commercial products co-condensation of two of these halides may be effected. For example, ethylene dichloride and dichloroethyl formal may be used together, the latter serving especially to improve low temperature properties of the elastomer. Abroad, glycerol dichlorohydrin and, reportedly in Japan, ethylene diglycoside are also used as intermediates. On stretching, some of the elastothiomers give x-ray diffraction patterns which indicate a more or less crystalline fiber structure, but in none is there evidence of orientation.

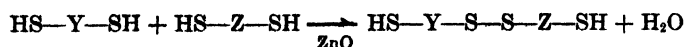
Compounding and Vulcanization

The elastothiomers can be vulcanized by heating to about 140°. Oxidizing agents are effective curing agents, typical examples being dinitrobenzene, trinitrobenzene, and benzoyl peroxide. Vulcanization is inhibited by such reducing agents as pyrogallol and zinc dust. In commercial practice, the vulcanizing agents employed are metallic oxides, chiefly zinc oxide, although others like cupric oxide and lead peroxide may be

Table 131. Unit Polymers of Sulfides ^{a1}

Unit of Polymer	Approximate Physical State
—CH ₂ S—	Powder
—CH ₂ SS—	Powder
—CH ₂ SS— SS	Rubber-like
—CH ₂ CH ₂ S—	Powder
—CH ₂ CH ₂ SS—	Powder
—CH ₂ CH ₂ SS— SS	Rubber-like
—CH ₂ CH ₂ CH ₂ S—	Powder
—CH ₂ CH ₂ CH ₂ SS—	Powder
—CH ₂ CH ₂ CH ₂ SS— SS	Rubber-like
—C ₂ H ₄ OC ₂ H ₄ S—	Powder
—C ₂ H ₄ OC ₂ H ₄ SS—	Rubber-like
—C ₂ H ₄ OC ₂ H ₄ SS— SS	Rubber-like
—C ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ S—	Powder
—C ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ SS—	Rubber-like
—C ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ SS— SS	Rubber-like
—CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ SS—	Rubber-like
—CH ₂ CH ₂ SCH ₂ CH ₂ SS—	Rubber-like

used. A trace of moisture is necessary in order to allow for curing by metal oxides which, in this instance, function as mild oxidizing agents. A completely satisfactory explanation of vulcanization of elastothiomers has not yet been propounded. It has been hypothesized that the end groups of the chains are mercapto radicals and that oxidation during vulcanization may involve coupling of chains by condensation of the terminal groups in the following manner:



Cross-linkages between chains may also be built up by formation of metallo-organo complexes. Ten per cent of zinc oxide is commonly recommended for cure. The rate of vulcanization is independent of the amount of oxide used, but less than five per cent is ineffective, while any excess over ten per cent serves merely as a filler. The change in stress-strain relationships brought about by vulcanization is shown in Figure 258.

It is not possible to cure elastothiomers to ebonite-like materials, although some of the non-elastomeric thioplasts fall in the category of solid plastics.

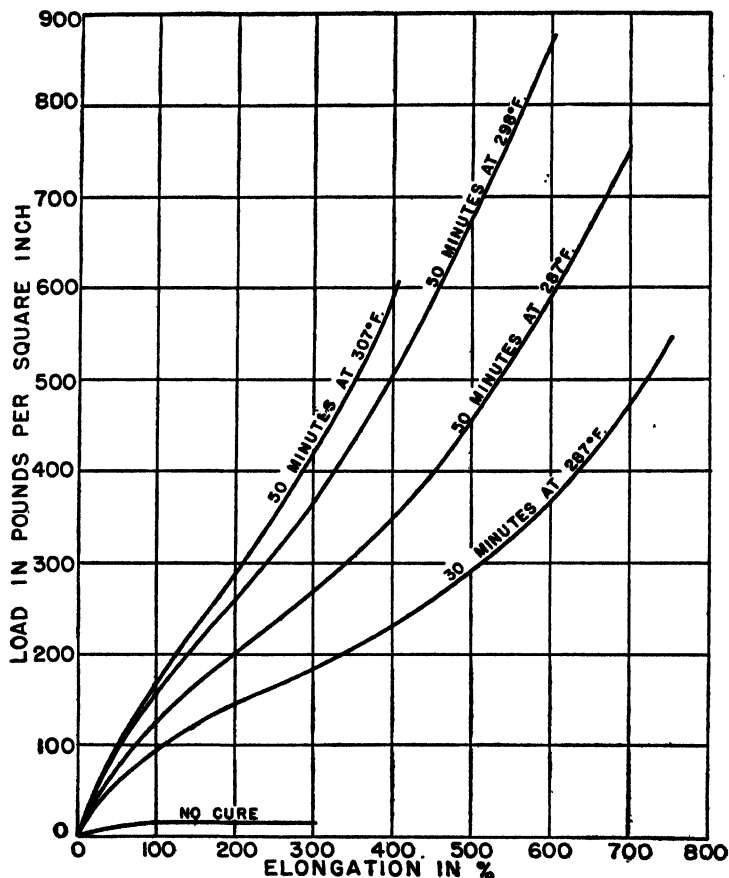


Figure 258. Stress-strain curves for vulcanized polysulfide elastomer $(-\text{O}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-)_n$. Compounding formula:

Elastomer	100.0	parts by weight
Zinc oxide	10.0	
Carbon black	20.0	
Stearic acid	0.50	
Benzothiazyl disulfide	0.25	
Diphenylguanidine	0.10	

(Patrick ⁷⁰)

Although sulfur does not bring about vulcanization of these products, it does act as an accelerator.

The elastothiomers can be compounded in much the same manner as

natural rubber. Semi-reinforcing and soft carbon blacks greatly enhance physical properties and are almost universally employed. Forty per cent of black, based on the elastomer, is about optimum in the case of "Thiokol" FA, yielding tensile strengths in the order of 1200 lbs per sq in and elongations of 500 to 600 per cent. Stearic acid is used in amounts up to one per cent to help disperse these reinforcing agents.

For white stocks, zinc oxide may be used.

The elastothiomers are relatively little affected by softeners such as oils and natural resins, but they are subject to chemical plasticization by milling with certain of the usual natural rubber accelerators. Benzothiazyl disulfide ("Altax") is especially active in this respect, as little as 0.25 per cent exhibiting marked plasticizing action while 0.35 per cent causes too great softening for most purposes. This chemical plasticizer is most effective in the presence of diphenylguanidine. Thiuram disulfides behave similarly.

Properties

The elastothiomers are the neurotic members of the family of commercial elastomers. They possess extremely good physical properties in some respects and very disagreeable ones in others. They exhibit unequaled solvent resistance. They are unexcelled in gas impermeability. They possess good aging characteristics and exceptional resistance to ozone. Special grades for low temperature service are available which not only retain rubber-like properties at temperatures as low as -60° F, but which can also be used as insoluble plasticizers to improve low temperature properties of other elastomers such as polychloroprene (neoprene) and butadiene-acrylonitrile copolymers ("Buna" N).

On the other hand, they possess a disagreeable odor and liberate a lachrymatory gas on heating or milling. Although newer grades are somewhat less objectionable than the earliest products from this point of view, the opinion of a manufacturer's representative that they possess an odor reminiscent of sweet violets has yet to be substantiated by factory hands! Among other unfavorable properties of these elastomers should be mentioned the fact that with certain grades, at least, stiffening occurs with age. This behavior is less marked after vulcanization than before. Crude polyethylene tetrasulfide, for example, becomes as hard as a rock on standing at room temperature. Newer grades, such as "Thiokol" FA, are vastly improved, although some stiffening is still encountered in GR-P, a grade of "Thiokol" N prepared from a mixture of ethylene dichloride and propylene dichloride. Relatively poor heat resistance, cold flow, lack of abrasion resistance in *tiré* treads, and low tensile strength are other unfortunate shortcomings of these materials.

In such applications as gaskets and cements, some of these properties like cold flow are definitely advantageous.

Insofar as tensile strength is concerned, 1500 lbs/sq in represents the upper limit of properly compounded elastothiomers currently available.

In solvent resistance the elastothiomers are outstanding. Their solubility varies somewhat according to structure, but they are generally insoluble in hydrocarbons, esters, alcohols, and most other organic solvents. Even carbon disulfide swells them but slightly. Their strength is little affected by prolonged immersion in oils and miscellaneous liquids. Ethylene dichloride is among the rare solvents which will dissolve them and which can be used to prepare solutions. They do not show much tack. In building up plies, naphtha and other solvents used with natural rubber should not be employed because they decrease tack and adhesion. Stocks should be moistened with mixtures of ethylene dichloride and chlorobenzene instead. For bonding to rubber, an intermediate tie-gum should be used containing an admixture of elastothiomers and well masticated natural rubber.

The permeability of polysulfide derivatives of dichlorodiethyl ether is shown in Table 132. The helium to hydrogen ratio is about 0.64, similar to that shown by rubber.

Table 132. Permeabilities to Hydrogen of Unsupported Films of Polysulfide Derivatives of Dichlorodiethyl Ether ⁷⁵

	Average Thickness		Permeability		Specific Permeability
	(cm)	(in)	(l/sq m/24 hr)	(cu ft/sq yd/24 hr)	
Disulfide derivative	0.030	0.012	0.6	0.018	12.5
	0.025	0.010	0.8	0.024	13.8
	0.017	0.007	1.4	0.041	16.2
	0.015	0.006	1.5	0.044	14.6
	0.011	0.004	2.2	0.065	16.8
Tetrasulfide derivative	0.033	0.013	0.2	0.006	4.5
	0.024	0.010	0.4	0.012	6.6
	0.019	0.008	0.6	0.018	7.9
	0.016	0.006	0.8	0.024	8.8
	0.009	0.004	1.2	0.036	7.5
Rubber	0.030	0.012	10.0	0.295	208
	0.025	0.010	14.2	0.419	246
	0.018	0.007	20.0	0.590	250

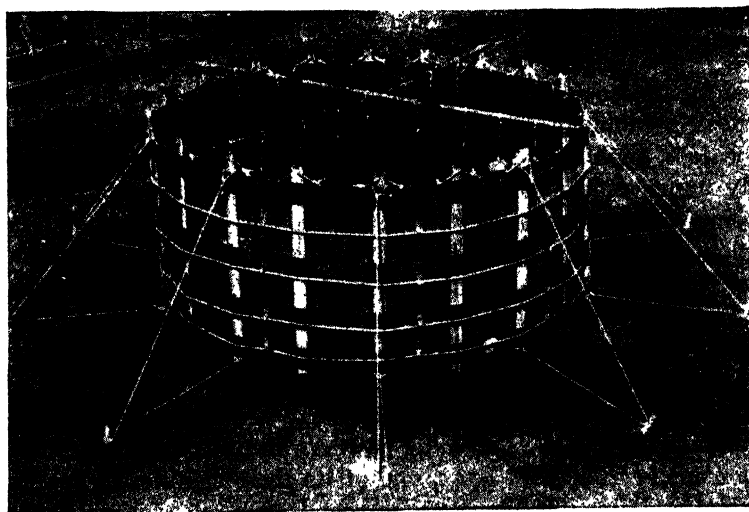
Applications

The most important uses of elastothiomers are based on their solvent resistance and impermeability to gases. They are utilized in gasoline hose in automobiles and service stations, in oil-loading hose, in printers' rolls and newspaper blankets, and as the hydrocarbon-resistant lining of bullet-proof gas tanks for airplanes, military portable fuel depots, and box-cars



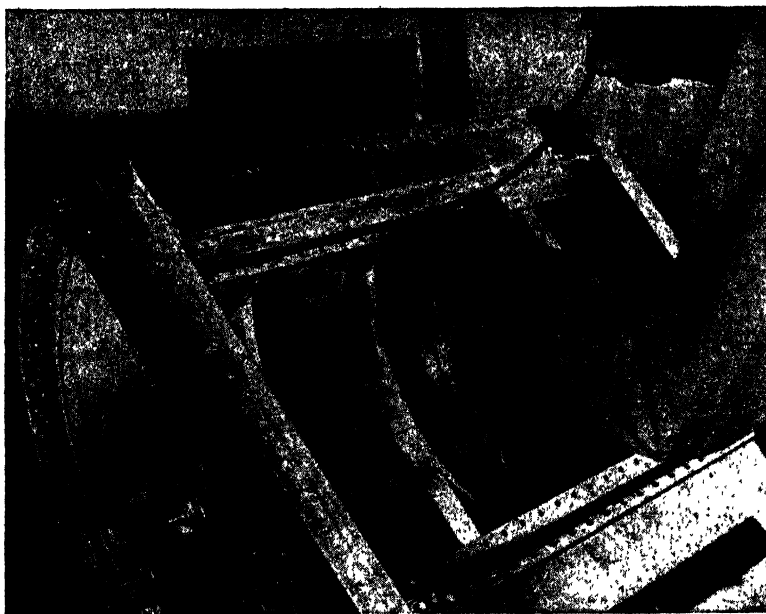
Courtesy Thiokol Corp.

Figure 259. "Thiokol" oil suction and discharge hose used for loading and unloading cargoes of gasoline, aromatic blended gasoline, and other solvents.



Courtesy Thiokol Corp.

Figure 260. Gasoline field storage tank utilizing "Thiokol" oil-proof synthetic rubber for construction of cell.



Courtesy Thiokol Corp.

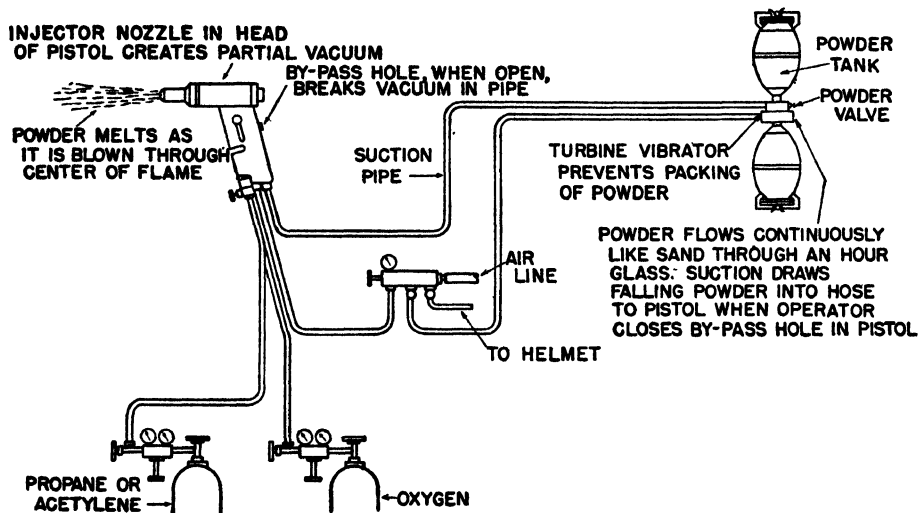
Figure 261. This "Thiokol" FA putty, used to seal the joints of aluminum airplane gas tanks to prevent fuel leakage, forms a permanent bond with the metal, but does not stick to the fingers during application and can be put on with bare hands. The oil and gasoline resistant material retains its flexibility and sealing properties even at subzero temperatures.

adapted for transportation of fuel oil. They are also used in paint spray hose, electric cable covering, and miscellaneous diaphragms and gaskets. For the last application, paper coated with elastothiomers serves admirably under difficult conditions of solvent and temperature, plastic flow being a valuable characteristic, in this case, to ensure satisfactory sealing. Asbestos impregnated with "Thiokol" serves as a flexible seal for floating roofs of gasoline storage tanks, while "Thiokol" putties are utilized to seal cracks and seams in aluminum airplane wings used as fuel cells. The low permeability of elastothiomers adapts them to use in balloon fabrics.

"Thiokol" is available not only in the form of crude for rubber processing equipment, but also as molding powders and solutions. An important development is "Thiokol" latex, one of its most significant applications being in the lining of Navy underground gasoline storage tanks and concrete tankers. For such use, the concrete is first sprayed with water to prevent complete absorption of subsequent layers of latex. Then two coats of "Thiokol" latex are applied, the surface lined with light cotton

sheeting; a third coat of "Thiokol" latex is then applied. Finally several finishing coats complete the job.

"Thiokol" is also available in powdered form for flame-spraying with the Schori gun, as illustrated in Figure 262. Most important application of flame-sprayed "Thiokol" is in coating steel shafts fitted with bronze propellers for use in mine sweepers, destroyers escorts, and other vessels. Corrosion caused by electrolytic action between dissimilar metals in sea



Courtesy Product Engineering

Figure 262. Diagram of the Schori flame-spraying equipment and its operation. This apparatus was developed to spray powdered metal as a protective coating. It is now also used for the spraying of "Thiokol" and various thermoplastics.

water is thus eliminated. Other uses of flame-sprayed "Thiokol" include linings of salt water pipeline valves, bearings, and low pressure condenser plates.

Commercial Products

Elastothiomers are known in the United States under the trade-mark "Thiokol." It should be noted, however, that use of this trade-mark has not been limited to these materials, but has covered other products such as "Thiokol" RD, a butadiene-acrylonitrile copolymer formerly made by the Thiokol Corporation. "Thiokol" A, B, D, F, FA, and ST are elastothiomers. A is polyethylene tetrasulfide; B is produced by reacting β,β' -dichlorodiethyl ether with sodium tetrasulfide. D is made from B by reaction with caustic soda, whereby the corresponding polydisulfide is formed. The composition of F has not been announced. It is especially

valuable because of its retention of rubber-like qualities at low temperature and is probably a condensation product of sodium tetrasulfide with both ethylene dichloride and dichloroethyl formal. Type FA, also apparently derived partly from the formal, is an improvement from the point of view of odor and lessening of lachrymatory gases during processing. Type ST, a new polysulfide elastomer which is reported to come from the formal and trichloropropane, possesses markedly superior resistance to cold flow as compared to earlier varieties. It retains flexibility at -60° F without added plasticizers and can be used under higher operating temperatures as well.

The Government synthetic rubber program resulted in the production of GR-P (Government rubber-polysulfide), formerly designated "Thiokol" N. It is based on a mixture of ethylene dichloride and propylene dichloride.

Similar products are made abroad. In Germany, "Perduren" G and H are manufactured from dichlorodiethyl ether and dichloroethyl formal, respectively. Another grade, like the British "Vulcaplas," is produced from glycerol dichlorohydrin. The English "Novoplas" A is comparable to "Thiokol" B and "Perduren" G. A Japanese product, "Thionite," is reportedly made from ethylene diglycoside by reaction with sodium tetrasulfide. Other materials of this category include the Belgian "Ethanite," Russian "Resinit," and Japanese "Hydrite."

Current domestic production is in the order of 24,000 long tons per annum. Average price is about 35 cents per pound.

Plastic Sulfur

A unique application of "Thiokol" has been found in plastic sulfur. Developed during the 'thirties by W. W. Duecker at Mellon Institute, this product is sold under the trade name "Tegul." It can be applied in molten condition and is used as an acid-proof cement for pickling tanks, chemical process equipment, and sewers. It is also used in the construction of acid-proof floors and in laying brick roads.

Plastic sulfur is produced by first milling or otherwise admixing phosphorus pentasulfide or other metalloids polysulfide with "Thiokol," then dissolving the plasticized elastothiomer in molten sulfur. On cooling, the sulfur retains its amorphous, plastic condition. Various degrees of plasticity can be obtained, depending on the proportions of the ingredients.

Elastoplastics

Numerous thermoplastics have been compounded with various plasticizers to give more or less rubber-like materials. In addition to these

products, specific members of several classes of plastics, such as the alkyds and acrylics, have been found which of themselves possess rubbery properties. These products have been listed on p. 555 and are discussed at appropriate points throughout this text.

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Chapter 21

Rubber Derivatives

By far the most important uses of rubber are those based on its elastomeric character. These applications, utilizing soft vulcanized rubber for the most part, have been discussed briefly in Chapter 20. Use of rubber as a chemosetting plastic in the production of ebonite has also been considered there. In addition to soft and hard vulcanized rubber, however, there are a number of other types of resinous derivatives of this material which have important specialty uses. Their volume is small, although it was steadily increasing before World War II interrupted further expansion. In 1939, chlorinated rubber, for example, is reported to have been produced at the rate of something over a million pounds a year. At that time, there was but a single American firm making this product, and full-scale plant operations had begun only two years before. A second producer entered the field shortly before Pearl Harbor.

The resinous derivatives of rubber to be discussed in this chapter are, for the most part, thermoplastic. They include isomerized rubber, rubber hydrochloride, chlorinated rubber, and oxidized rubber.

The Nature of Rubber

Crude rubber nominally contains about 92–94 per cent of high molecular weight hydrocarbons. The remainder is a mixture of proteinaceous material, acetone-soluble substances—including higher fatty acids and a variety of more or less resinous materials, ash, and moisture. By specific methods of treating latex during coagulation, it is possible to produce deproteinized rubber for special applications. The nitrogen content of the coagulum is thereby reduced from about 0.05 per cent to 0.015 per cent or less. Even as low as 0.006 per cent can be obtained. Deproteinized rubber tinted with eosin for identification purposes is commercially available and has been discussed in Chapter 20.

For many years the structure of the rubber hydrocarbon was a problem which called forth a vast amount of research on the part of a large number of eminent chemists. Even today, although its basic nature is understood, much remains to be clarified. It is a striking tribute to

or by addition of a small amount of butyl alcohol or an aliphatic amine. It seems probable that gel rubber is composed of chains like those described above, cross-linked here and there with oxygen bridges or some other type of bond. A very slight amount of cross-linking would account for this behavior.

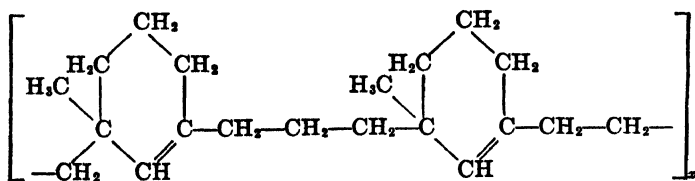
Mechanical mastication of rubber results in molecular breakdown. The average molecular weight of milled rubber is much less than that of untreated material. This subject has been discussed further in Chapter 20. Decrease in molecular weight is accompanied by far-reaching physical alterations, especially increased plasticity and decreased viscosity of solutions. Similar reduction in the size of the rubber molecule can be effected by other means, also. In general, wherever the rubber hydrocarbon is subjected to a vigorous chemical reagent, it is broken down. The more vigorous the conditions of reaction and the more violent the reagents, the greater is the decomposition.

Chemical reactions of the rubber hydrocarbon, for the most part, are determined by its unsaturation and its proclivity for decrease in molecular size.

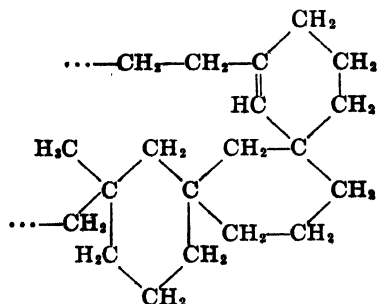
Isomerized Rubber

A number of treatments are known whereby the rubber hydrocarbon can be converted into isomers having quite different properties. Synthetic methyl rubber (polydimethylbutadiene), although no longer a commercial product, acts in the same way. Certain other synthetics such as polyisoprene and even GR-S behave similarly.

If, for example, rubber is converted to rubber hydrochloride which is then treated with zinc dust in toluene solution, hydrogen chloride is eliminated in the final step and the product has the same empirical formula as rubber (C_5H_8)_x, but is only half as unsaturated. It is called monocyclorubber and has been assigned the following formula by Staudinger:



If this reaction is carried out in the presence of hydrogen chloride a still different product called polycyclorubber is obtained. This substance shows only a fraction of the unsaturation of the original rubber hydrocarbon. For it, the following structure has been suggested:



Both of these products are thermoplastic high polymers, neither of which possesses rubber-like character. Their properties vary somewhat with the details of the preparative methods used. Upon simple heating of rubber *in vacuo*, decomposition into smaller aggregates occurs, some of the larger ones being cyclized.

If rubber is treated with other chemicals, it can be converted into still other thermoplastic hydrocarbons which differ in their properties according to their mode of formation. They all possess the empirical formula $(C_5H_8)_x$ and show less unsaturation than the original rubber hydrocarbon.

All of these various products are called rubber isomers or cyclorubbers and the processes employed to make them are usually denoted "cyclization." There appears to be very little evidence supporting the various cyclic structures advanced for any of these substances, including Staudinger's cyclo- and polycyclo-rubbers. Indeed, it has been maintained in some quarters that cyclization does not occur at all in these reactions. There is, however, still less evidence for this argument and the preponderance of current opinion favors some sort of cyclic structure.

These rubber isomers are reactive toward the same chemicals that act upon rubber itself. Hydrochloric acid, chlorine, oxygen, perbenzoic acid, and ozone react with them. As in the case of rubber, oxidation can be greatly reduced by antioxidants. Although they can be vulcanized, the vulcanizates so formed have no particular merit and, except for limited application in hard rubber or incidental formation in certain bonding procedures, they do not appear to be of commercial utility.

Action of Sulfuric Acid and Its Derivatives on Rubber. Sulfuric acid and some of its derivatives such as chlorosulfonic acid react vigorously with rubber, either alone or in solution. The products are usually insoluble and high-melting. H. L. Fisher, however, found that the reaction can be moderated to yield soluble, more or less inelastic, thermoplastic rubber isomers by milling the acid into the rubber and subse-

quently heating the resultant mixture under controlled conditions. Still better, a considerable number of organic sulfonic acids of both the aliphatic and aromatic series can be used in the same manner. So also can their corresponding sulfonyl chlorides. Among these isomerizing agents are *p*-phenolsulfonic acid, *p*-toluenesulfonic acid, β -naphthalene-sulfonic acid, benzenesulfonic acid, chloro- and nitro-benzenesulfonic acids, sulfobenzoic acid, Syntans, Twitchell reagents, ethanesulfonic acid, sulfonated kerosene, diphenylamine sulfate, and dimethyl sulfate. Amino sulfonic acids are usually not effective. These reagents can subsequently be washed out with water, although they are partially destroyed during reaction, with attendant liberation of sulfur dioxide. Many other chemicals can be used to cause similar isomerization. Particularly efficient are the anhydrous iodides of amphoteric metals.

Some ten parts of isomerizing agent to 100 parts of rubber are customarily used, but more or less than this amount may be employed, according to the character of the product desired. Heating is carried out for several hours at temperatures varying from 100 to 145°. After a preliminary period of heating, the length of which varies with the nature of the reagent and the amount used, a vigorous exothermic reaction occurs. The products are normally dark colored, but become white upon purification. They are soluble in the usual rubber solvents and are similar in physical appearance to gutta percha, balata, or shellac, depending upon the conditions of reaction. With 7.5 parts of *p*-phenolsulfonic acid and 100 parts of rubber, for example, heated to about 140° for six hours, the product resembles gutta percha; with 10 parts of reagent, heated in bulk, it resembles shellac. In the latter instance, if the milled product is sheeted into slabs one-half inch thick and heated in soapstone for 48 hours at 110°, the resulting isomer is then similar to balata.

The products obtained by isomerizing rubber with sulfonic acids are known as thermoprenes, to which the suffixes GP, HB, and SL are attached to denote their respective resemblance to gutta percha, hard balata, or shellac.

Typical physical properties are given in Table 133.

Although more resistant to decomposition by heat than natural rubber, the thermoprenes are thermoplastic and should not be used where heat-resistance is a factor. They are approximately 57 per cent as unsaturated as rubber and are more resistant to oxidation than the latter. They are also resistant to alkalis and mineral acids, with the exception of nitric acid. They dissolve in the usual rubber solvents, including gasoline, toluene, benzene, carbon tetrachloride, and turpentine.

These rubber isomers are used principally in the formulation of ad-

Table 133. Physical Properties of Thermoprenes^a

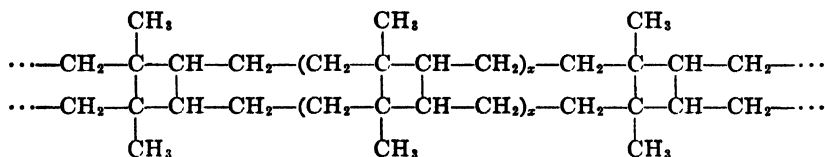
Property	Thermoprene GP	Thermoprene HB	Thermoprene LS
Specific gravity (rm. temp.)	0.980	0.993-1.016	0.993-1.003
Tensile strength (lbs/sq in at 22°)	2600	2300-4800	660
Elongation at break, per cent	27	1.3-29.8	0.6
Impact strength (in lbs/sq in at 0°)	50	20.8-42	1.4-6.6
Ultimate compressive strength (lbs/sq in)	5400	3850-10,600	7100-9000
Ultimate transverse strength (lbs/sq in at 21°)	8100	4800-7200	1600-2140
Cold flow, per cent (50,000 lbs load at rm. temp.)	38.6	17.3-38.2	22.8-34.3
Dielectric strength (volts/mm)	47,500 (0.91 mm thick)	50,000-55,200 (0.94 mm thick) (1.07 mm thick)	51,800-53,200 (0.76 mm thick) (0.89 mm thick)
Softening temperature (° C)	Room Temperature	65-77	

hesives and paints. They serve as the basis for "Vulcalock" cement which gives an exceptionally strong bond between rubber and steel or other smooth surfaces. The "Vulcalock" process of bonding rubber to metal has proved to be of vast importance in the construction of rubber-lined steel tanks and vats, tank cars, drums, barrels, and other corrosion-resistant equipment.

The thermoprenes are also the base of a series of rapid-drying acid- and alkali-resistant paints formulated without oils or nitrocellulose. These paints, known under the trade name "Acidseal," yield films which possess excellent adhesion to properly prepared metals and other surfaces. Films are hard, firm, durable, and exhibit some of the elasticity of rubber. They possess good resistance to moisture and most chemicals of acidic or alkaline nature. They are, of course, soluble in rubber solvents and, because of the thermoplastic nature of the thermoprenes, they soften at temperatures above 175° F. These paints are available in several colors as both primer and top coats and can be applied by either brushing or spraying. Unlike rubber, good brushing properties are retained when the thermoprene solids content of a paint is as high as 20 per cent, or even more. Innumerable industrial applications have been made where corrosion resistance and durability are essential.

Action of Metallic Halides on Rubber. If dissolved in benzene, ether, or other suitable solvent, the rubber hydrocarbon adds many metallic and metalloid halides which customarily effect polymerization of vinyl compounds, such as stannic chloride, titanium tetrachloride, ferric chloride, and antimony pentachloride. Upon treatment of the resultant addition product with alcohol or acetone, elimination of the halide occurs with formation of a rubber isomer which is capable of recombining

with stannic chloride, for example. Similar results can be obtained by use of boron trifluoride, fluoroboric acid, or halogenated acids of tin like chlorostannic acid ($\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$) and chlorostannous acid ($\text{HSnCl}_3 \cdot 3\text{H}_2\text{O}$). The chemicals just enumerated can be reacted with rubber directly on the mill, or in benzene solution. In all these instances, the product is less saturated than the original rubber hydrocarbon. The following structure has been suggested for the product without proof:



It seems highly improbable that this structure actually corresponds to the facts. Formation of cyclobutane rings in such a reaction, especially where one of the cyclic bonds is established between two tertiary carbon atoms, appears most unlikely. Moreover, it is not probable that only two rubber chains would be crosslinked by such a reaction.

Whatever the structure of the resulting products, operations of this kind are employed commercially in the manufacture of rubber isomers sold under the trade name, "Plioform." These materials vary in physical appearance from those resembling balata to others more similar to hard rubber. As reaction advances in benzene solution, the viscosity decreases progressively, so that the point at which refluxing should be stopped to yield a rubber isomer having the particular properties required for a given application can be determined from the viscosity of the solution.

"Plioform" resins are thermoplastic, substantially non-elastic, and resistant to most acids and alkalis. They are much more resistant than hard rubber to nitric acid and are practically unaffected by this acid in concentrations up to 60 per cent. At 120° F, cold flow is less than that of hard rubber. These resins are insoluble in such oxygenated solvents as acetone, alcohol, and ether, but are soluble in the usual rubber solvents like benzene. Compounding with titanium dioxide makes them more oil resistant. Gel-rubber gives a product which is relatively insoluble in benzene and less readily oxidized than isomers of sol-rubber. "Plioform" resins can be softened with many of the common plasticizers. In surface coatings, raw tung oil is particularly effective. Such preference for unboiled oil stands in marked contrast to customary paint and varnish technique.

Properties of commercial grades of "Plioform" are listed in Table 134.

These rubber isomers have found application in resinous corrosion-resistant linings for steel tanks and vats, in "Pliolite" acid- and alkali-

Table 134. Physical Properties of "Plioform"^a

Specific gravity	1.06
Odor	None
Taste	None
Softening point, °F:	
No. 20 "Plioform"	220
No. 40 "Plioform"	175-195
Cold flow ^a (in per in of length)	0.00035
Molding temp. °F:	
No. 20 "Plioform"	310
No. 40 "Plioform"	260
Coefficient of thermal expansion	0.00008
Mold shrinkage (in per in)	0.0035
Resistance to discoloration by light	Good
Surface resistivity (ohms per linear in):	
At 90% relative humidity	1×10^{11}
At 75% relative humidity	1×10^{12}
Tensile strength, lb/sq in	4000-5000
Compressive strength, lb/sq in	8500-11,000
Flexural strength, lb/sq in	7000-9000
Impact strength (Izod notched), $\frac{\text{ft-lb}}{\text{width} \times \text{thickness}^a}$	2.5-6.2
Water absorption (24-hr immersion), %	0.03
Resistance to conc. acid	Good ^b
Resistance to strong alkali	Good

^a At 2000 pounds per square inch pressure and 120° F^b Except strong nitric and strong sulfuric

resistant paints, especially recommended as metal primers and concrete enamels, and in thermoplastic molding compounds which have been used, compounded with rubber for example, in the manufacture of golf ball coverings. Laminated "Plioform" products can also be produced. Just before Pearl Harbor, developments were announced relating to the application of "Plioform" in the outer shell of non-metallic airplane gas tanks. If pierced by bullets, unlike aluminum, the "Plioform" does not tear and flare out into the interior bullet-proof liner thereby preventing closure of the hole.

Recently, investigations have been directed toward the production of cyclized derivatives of synthetic polymers and copolymers of diolelins. Table 135 lists properties of isomerized GR-S.

During World War II, Goodyear successfully developed a replacement for "Pliolite" in the form of cyclized synthetic polyisoprene. The cyclized material is made from this polymer by the same process as was formerly used in producing natural rubber "Pliolite." It is called "Pliolite" S-1 and has found many of the same usages in industry as the former material. For example, it is used in combination with wax in hot melt paper coatings, in coatings for rigid surfaces, and in combination with GR-S and other elastomers for rubber compounding adapta-

Table 135. Properties of Cyclized GR-S *

Specific gravity	0.99–1.03
Softening point	55–105°
Solubility	Aromatic hydrocarbons, chlorinated hydrocarbons
Iodine number:	
Original GR-S	350
Soft cyclo GR-S	200
Hard cyclo GR-S	180–60
Compatibility	Paraffin, GR-S

Moisture vapor transmission on glassine (compounded with 10 % paraffin):

<i>Coating weight</i>	<i>M.V.T.</i>
lbs/ream	(gms/sq m/24 hrs)
0.7	4.08
2.4	1.79
3.5	1.09

tions. It has been introduced as a base for acid- and alkali-resistant paints and, for such solution applications, possesses the advantage over natural rubber "Pliolite" of exhibiting lower viscosity at the same solids concentration in all solvents.

"Reanite" and "Cycleweld," two new adhesives developed for rivetless bonding of metal sheets and other smooth surfaces, have been said to be based on rubber compounds, presumably rubber isomers. Little information concerning the nature of these materials has, however, been released and several different types of "Cycleweld" exist. These products, particularly the latter, rendered excellent military service, especially in the aircraft industry.

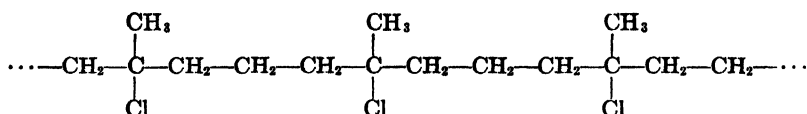
Rubber Hydrochloride

Inasmuch as rubber is highly unsaturated, it is capable of adding hydrogen chloride at the double bonds. This reaction can be carried out in several ways. Sheets of rubber can be exposed to the action of hydrogen chloride dissolved in liquids like ethyl acetate which swell, but do not dissolve the rubber hydrocarbon. Thin sheets of rubber can also be exposed to liquefied hydrogen chloride or to gaseous hydrogen chloride under pressure. Again, gaseous hydrogen chloride can be passed into solutions of rubber in benzene, toluene, chloroform, or other chlorinated solvents. In the last instance, carbon tetrachloride is not very satisfactory because of the insolubility of hydrogen chloride therein. In all cases, the rubber should preferably be milled before reaction and the hydrogen chloride, as well as any reaction media employed, should be kept dry. In order to minimize molecular breakdown and other secondary

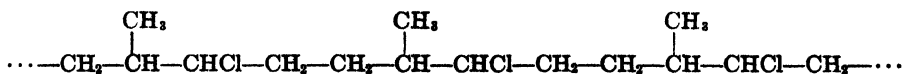
reactions, hydrochlorination should be carried out in the cold, preferably at temperatures below 5°. Conditions as low as -35° and still lower have been used. The product can be isolated by evaporation of the solvent, by steam distillation thereof, or by precipitation with methanol or ligroin.

Rubber hydrochloride is not truly thermoplastic, inasmuch as it decomposes before it melts. Evolution of hydrogen chloride is conspicuous at 145° and vigorous at 185°. Depending upon the method of manufacture, particularly the presence of moisture during reaction, decomposition may occur at considerably lower temperatures—even as low as 40°. Films of rubber hydrochloride tend to become brittle with age, but can be stabilized by incorporation therein of various organic and inorganic compounds of more or less basic nature, such as magnesium oxide, hexamethylene tetramine, triethylene tetramine monostearate, or benzyl trimethyl ammonium stearate. Dipentene and pine oil also tend to stabilize this resin.

The formula commonly ascribed to rubber hydrochloride is as follows:



Although the product is somewhat unstable, like all macromolecular compounds containing chlorine, the degree of instability, especially towards water and alkalis, is very much less than might be expected from a substance comprising such a multiplicity of tertiary chloride groups as depicted by the above formula. There would, therefore, appear to be reasonable doubt as to whether or not this formula actually describes rubber hydrochloride. Inasmuch as the rubber hydrocarbon is very sensitive to oxygen and inasmuch as Kharasch has shown that Markonikoff's rule for the addition of hydrogen halides to relatively simple olefins is sometimes inverted by the presence of peroxides, it would seem plausible that the structure of rubber hydrochloride might be more accurately represented by the following formula:



Both of the above formulas, however, disregard the possibility of isomerization which most likely proceeds to some extent during hydrohalogenation. The chlorine content of rubber hydrochloride is usually about 30.5 per cent, as contrasted with the theoretical of 33.9. This fact, together with x-ray data, emphasizes the probability of some cyclization.

Rubber hydrochloride has a density of 1.16. It is colorless, odorless, tasteless, and unaffected by mold and insects. It is soluble in chloroform and chlorinated solvents in general, but relatively insoluble in many other liquids including alcohol, ether, benzene, and carbon disulfide. It is very difficultly flammable and is resistant to fatty oils and greases, and to dilute aqueous alkalies and acids, except nitric.

Films of rubber hydrochloride can be cast from solution or calendered on heated rolls. Filaments can also be spun by either dry or wet processes, in the latter instance with the aid of alcohol, acetone, or other coagulating liquid. For wrapping purposes, films should contain from 28 to 31 per cent of chlorine.

Before Pearl Harbor, this resin appeared on the market under the trade names "Pliofilm," "Tensolite," and "Marbon."

"Pliofilm" was produced as a nearly colorless, transparent packaging material. It was also available in a variety of colors, both transparent and opaque, including metallic finishes. It was manufactured in several thicknesses, from one to two and a half mils, and in several qualities depending upon the presence or absence of plasticizer and the amount present. Widths were made up to 40 inches. It can be heat-sealed at temperatures between 105 and 130° or, by conjoint use of a solvent like toluene, at lower temperature, down to 70°. It can also be bonded with suitable adhesives and lends itself readily to printing.

Films of rubber hydrochloride are not only grease-proof, but also moisture- and waterproof. They possess good dimensional stability so that wrinkling does not occur within the humidity range of 15 to 90 per cent. They retain a limited degree of rubber-like qualities. Although not as strong as transparent cellulose films, they are more tear-resistant and pliable. They can also be stretched to some extent, so as to conform to irregular surfaces which they may envelop. They are not readily punctured. They are relatively resistant to low temperatures.

Prior to Pearl Harbor, films of rubber hydrochloride had gained considerable favor as decorative and packaging material, in bags for certain foodstuffs such as cold meats and pickles, and in such articles as raincoats, umbrellas, shower curtains, garment bags, and card table covers. For packaging foodstuffs, unplasticized film is preferred; for other applications such plasticizers as butyl stearate are used.

Brushes assembled from strips or monofilaments of rubber hydrochloride acquired utility as whisk brooms because of the static electric charge which they acquire upon frictioning, thus attracting dust particles. Based upon the same principle, similar brushes have attracted attention in massaging the body to alleviate pain.

Rubber hydrochloride films found an important military application

during World War II in extensible bags which could be used to enclose airplane engines during shipment. Such wrapping conformed closely to the shape of the engine, was tough, and protected the metal from corrosion, thus eliminating the necessity for greasing and degreasing operations.

The x-ray pattern of rubber hydrochloride shows it to be crystalline. Stretching or "racking," as it is called in the rubber industry, is therefore feasible, with consequent orientation of the molecular structures attended by increase of tensile strength and greater durability. Stretched rubber hydrochloride has been marketed for special applications under the trade name "Tensolite." Prior to the war it had achieved a measure of success in the packaging of foodstuffs.

Another application of rubber hydrochloride which began to develop shortly before the Japanese occupation of the Far Eastern rubber growing regions was in bonding agents for miscellaneous purposes. "Marbon" adhesives were of this general type.

Chlorinated Rubber

History. The earliest observation of the action of chlorine on rubber was made by the Frenchman, A. F. Fourcroy, in 1791 when he recorded the ability of chlorine water to precipitate rubber latex. Almost seventy years passed, however, before the nature of chlorinated rubber was recognized.

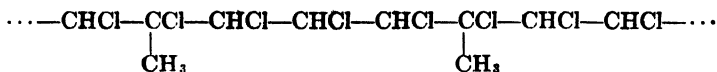
The first purposeful preparations of this rubber derivative were carried out by the Americans, G. A. Engelhard, R. F. H. Havemann, and H. H. Day who, in 1859, received the earliest of a number of British and American patents on the subject. During the next forty years, a considerable number of American patents were granted to various investigators in this field, while important scientific papers dealing with chlorinated rubber appeared in England. Finally, in 1915, the British chemist, S. J. Peachey, took out patents for the production of chlorinated rubber in solution and the manufacture of this substance under the trade name "Duoprene" was begun in England in 1917 by the United Alkali Company. "Duoprene" was marketed in the form of solutions and, to a limited extent, as a solid also. Its production was continued for a number of years until, with the formation of Imperial Chemical Industries, a new and improved form was placed on the market under the name "Alloprene."

In 1930, German production of chlorinated rubber began under the trade name "Tornesit," a designation which seems to have been derived from the town of Tornesch in which the plant of the manufacturer, the New York Hamburger Gummi-Waaren Co., was located. Other similar

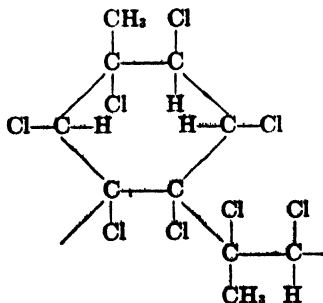
products under various names soon appeared in several countries. Domestic manufacture of chlorinated rubber on an extensive scale was first undertaken by Hercules Powder Co. who also marketed their product for a while under the name "Tornesit." Upon completion of a full-scale plant at Parlin, N. J., the name of this material was changed to "Parlon." Shortly before Pearl Harbor, manufacture of chlorinated rubber under the trade name "Raolin" was begun by the Firestone Tire and Rubber Co. by arrangements with the Raolin Corporation.

The early history of chlorinated rubber was characterized by conflicting praise and condemnation. With the introduction of improved processes of manufacture and methods of formulation, however, this semi-synthetic plastic has at length taken its place among the important resinous bases for surface coatings. During World War II, it found many highly important and specialized uses which dictated its continued production for essential military purposes, despite the shortage of natural rubber.

Chemistry and Manufacture. The reaction of chlorine with rubber results not only in addition of chlorine, but also in substitution. Indeed, substitution begins at once, whereas addition does not commence until later. The course of chlorination in solution at 60° is shown in Figure 263. Complete reaction occurs with introduction of approximately eight chlorine atoms per C₁₀ unit of rubber, corresponding to 68.3 per cent of chlorine in the finished product. It has been suggested that a unit of the fully chlorinated product corresponds to the formula



and several hypotheses have been proposed to explain both this formula and the relation between substitution and addition during reaction. None of these explanations has been proved and none takes into account the possibility of cyclization. Powers,¹⁷ however, has recently shown the following structure for a C₁₀ unit of chlorinated rubber:



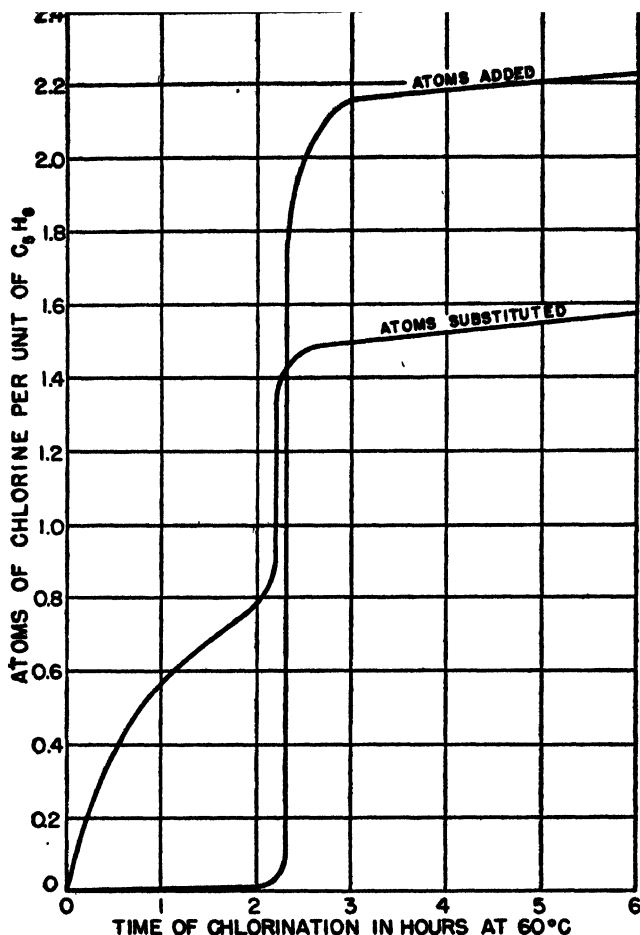


Figure 263. Course of chlorination of raw natural rubber at 60° . (Baxter⁸)

Commercial materials contain from 65 to 68 per cent chlorine, averaging between seven and eight chlorine atoms per C_{10} unit. The softening point of the product increases with increasing chlorine content, as shown in Figure 264.

Stability of the product increases markedly with increasing chlorine content. Chlorinated rubber can be stabilized by incorporation therein of various organic or inorganic materials of basic nature. Other types of acid-reactive chemicals, such as those containing ethylene oxide rings, also stabilize this resin. Propylene oxide, for example, is used to some extent to preserve its solutions. In general, however, satisfactory sta-

bility can be effected by careful control of chlorination conditions so that addition of antichlors which may cause discoloration does not correspond with usual industrial practice.

Numerous modifications of procedure can be used in the chlorinating process. Rubber latex can be treated with chlorine or sheet rubber can be chlorinated directly by either liquid or gaseous chlorine. Products from these reactions, however, are relatively insoluble in common solvents. In commercial practice, rubber is first dissolved in an appropriate solvent, preferably carbon tetrachloride. Chlorination is usually carried

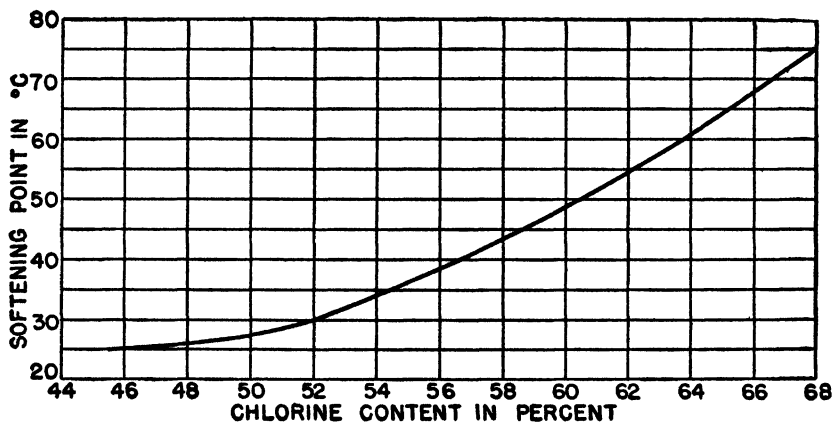


Figure 264. Relation between softening point and chlorine content of chlorinated rubber. (Nielsen¹⁵)

out in 4–5 per cent solution in glass-lined or lead-lined equipment. In the manufacture of "Parlon," hydrogen chloride from the reaction is removed in a tantalum absorber. Upon completion of the chlorination, the carbon tetrachloride solution is pumped into brick-lined precipitating tanks filled with hot water from which the solvent is distilled and the product is obtained as a granular precipitate which is washed with water, centrifuged, and dried. Among the factors determining stability of the resin are rate and temperature of chlorination. Industrial practice prefers temperatures near the boiling point of the solution. Low temperature chlorination yields unstable products. Careful control of temperatures and pressures is maintained throughout reaction which requires several hours.

Chlorinated rubber is produced in a number of different viscosities, depending upon the application for which it is intended. Viscosities available commercially, determined on a 20 per cent toluene solution at 25° in a capillary tube viscometer, are 5, 10, 20, 125, 1000 and 5000

centipoises. The control of viscosity is exercised primarily by reduction in the molecular weight of the rubber hydrocarbon prior to chlorination. This operation is accomplished by cold mastication of the solid rubber or, if desired, by mastication of rubber swollen with carbon tetrachloride. Still lower viscosities are obtainable by exposing solutions of milled rubber to elevated temperatures or to ultraviolet light, or by treating the solutions with such catalysts as copper stearate. Chlorination itself reduces the viscosity of the solution, while still further reduction may be brought about by passing the solution of chlorinated rubber through a colloid mill, or by exposing it to either ultraviolet light or an oxygen-containing gas in the presence of dissolved chlorine.

The resinous and proteinaceous content of natural rubber is a source of color in the finished product. It has also been maintained that these substances reduce the stability of this plastic. To eliminate them, the chlorinated rubber may be precipitated from solution by alcohol, or deproteinized rubber may be used as the initial material.

Properties and Uses. The properties of chlorinated rubber which are of the greatest importance are those which bear upon its principal use as a resinous base in the formulation of protective coatings. Unplasticized films of chlorinated rubber are too brittle to be of service and lack sufficient adhesion, but where suitably plasticized or combined with other resins, especially alkyds, it serves as an invaluable component of corrosion resistant finishes.

Unplasticized films tend to become somewhat brown upon exposure to ultraviolet light. It has been found that those plasticizers which very selectively absorb wave lengths approaching 2900 Å from the direction of 3100 Å exercise a stabilizing influence on chlorinated rubber films. Table 136 shows the relative discoloration under a carbon arc, corresponding to a hot June and July, of nineteen of the best plasticizers selected from a group of fifty tested by J. P. Baxter.

Chlorinated rubber is considerably more soluble than rubber hydrochloride. It is also much more soluble than either polyvinyl chloride or polyvinylidene chloride. Its unique solubility characteristics among highly chlorinated resins have developed for it an esteemed place in the formulation of corrosion-resistant paints. In general, aromatic hydrocarbons and many chlorinated hydrocarbons dissolve it. It is also soluble in esters and the higher ketones. Lower ketones swell, but do not dissolve it. It is dissolved by such miscellaneous solvents as nitrobenzene, the nitroparaffins, pyridine, and drying oils. It is insoluble in aliphatic hydrocarbons, aliphatic alcohols, ethylene glycol, glycerol, and turpentine. It is compatible with many oil-modified alkyd resins, coumarone-indene resins, certain modified phenolics, chlorinated biphenyls, chlorinated naphthalene, ester gum, and many natural resins. It is incompatible with polysty-

Table 136. Color Stability of Plasticized Chlorinated Rubber Films *

Plasticizer	Relative discoloration of film containing 23 %	log $\frac{2900}{3100}$	Relative volatility of plasticizer at 70°	Boiling range °C
Dimethyl phthalate	27	1.8	90	282-288
Diethyl phthalate	32	1.8	73	290-300
Butyl stearate	34	0.9	15	355-368
Dibutyl phthalate	36	2.3	20	325
Isobutyl phthalate	46	1.9	35	305-315
Diamyl phthalate	46	2.5	7	336-342
Diamyl oxalate	50	1.1	—	265
Amyl benzoate	53	1.0	—	261
Benzyl benzoate	67	1.3	97	323
No plasticizer	70	—	—	—
Triacetin	71	0.3	700	258
Butyl oleate	76	0.5	30	356-370 (decomp.)
Acetophenone	79	0.6	—	200-202
Ethylene glycol monoethyl ether	81	0.0	—	128-137
Dimethylcyclohexanol oxalate	101	0.6	—	—
Amyl tartrate	104	0.2	—	400
Chlorinated biphenyl	104	0.3	—	360-380
Triethyl citrate	109	0.4	57	—
Amyl lactate	117	0.4	—	210
Tricresyl phosphate	263	0.6	1	430-440

rene, the vinyl resins, and cellulose derivatives. Chlorinated rubber has found extensive application in conjunction with drying oils and modified alkyds, upon which it confers improved acid and alkali resistance, toughens films, and speeds drying time. The greatest use of this resin in recent years has been in combination with these resins.

Any of the common pigments can be used in chlorinated rubber finishes with the exception of most metallic powders which cause ultimate decomposition of the film, although aluminum powders have been used with very good results. Incorporation of pigments in chlorinated rubber solutions is assisted by such wetting agents as zinc naphthenate.

The tensile strength of unplasticized chlorinated rubber films averages from 6000 to 7000 lbs/sq in. Plasticization results in marked decrease of strength. Dibutyl phthalate, where added to the extent of 21 per cent of the weight of the finished film, yields strengths of about 3000 lbs/sq in, while slight increases of plasticizer above this proportion cause a further sudden decrease in strength; 23 per cent, for example, yields films which are soft, sticky, and show tensiles in the order of only 1500 lbs/sq in.

The resistance of chlorinated rubber to acids and alkalis has been shown in a striking manner by J. P. Baxter who determined tensile strength of unplasticized films before and after exposure to various reagents. His results are given in Table 137. Where plasticized films are required to possess excellent chemical resistance, non-reactive plasticizers, such as chlorinated biphenyl, should be used.

Table 137. Chemical Resistance of Unplasticized Films of Chlorinated Rubber^a

Temp.	Reagent	Strength	Duration of Test	Change in Weight	Tensile Strength lbs./in. ²	
					Before	After
20°	NaOH	100 g/l	168 hr	nil	5800	5900
		300 g/l	168 "	nil	5800	5800
		600 g/l	168 "	nil	5800	6000
	NH ₄ OH	0.880	168 "	nil	5400	6000
	HNO ₃	conc.	168 "	+ 2.3%	5400	5900
	HCl	conc.	168 "	nil	6500	5200
	NaClO	5% Av. Cl ₂	48 "	nil	5500	4700
		15% Av. Cl ₂	48 "	nil	5500	4400
	NaCl	10%	48 "	nil	5500	5500
		saturated	48 "	nil	5500	5200
	Acetic acid	glacial	168 "	+ 3.0%	5400	4000
	Formic acid	conc.	168 "	+ 3.3%	5400	4700
	Petrol ether	—	168 "	nil	5700	4600
40°	Water	—	48 "	nil	5700	4900
	NaOH	100 g/l	48 "	nil	6500	4900
		300 g/l	48 "	nil	6500	4600
		600 g/l	48 "	nil	6500	5500
	Petrol ether	—	48 "	nil	5600	2500
60°	HCl	10%	48 "	nil	5500	5300
		conc.	48 "	nil	5600	3700
	NaClO	5% Av. Cl ₂	48 "	nil	4800	4100
		15% Av. Cl ₂	48 "	nil	4800	3200
	NaCl	10%	48 "	nil	4800	4600
		saturated	48 "	nil	4800	4500

Properties of "Parlon" compiled from the manufacturer's literature are given in Table 138.

In this country, chlorinated rubber has been used exclusively as a component of various types of surface finishes. Limited application has been made abroad in thermoplastic molding compositions, spun wool, and expanded porous material for heat insulation.

For surface coatings, it is recommended (1) as the major ingredient, (2) in amounts up to 25 per cent as an addition agent to long oil-modified alkyds, and (3) in minor amounts of five to ten per cent in compatible finishes to improve properties and cut drying time.

It is used to protect chemical plant equipment, as a basis for concrete, masonry, plaster, stucco, and asbestos-cement board paints, to finish swimming pools, and for numerous other corrosion-resistant applications. In pigmented paints it was widely used in the 1939 New York World's Fair on exterior surfaces. Other applications of chlorinated rubber are made in alkali-resistant printing inks for such uses as soap wrappers, in adhesives, and in textile coatings. This resin is used to some extent in the bonding of rubber and synthetic rubbers to metal. It is said that one formulation of "Ty-Ply," a bonding agent for rubber-to-steel joints, comprises a mixture of chlorinated rubber and sulfur which establishes a strong union upon application of heat.

Table 138. Properties of "Parlon" *

White granular powder, producing almost white films. It is odorless, tasteless, non-toxic, non-flammable, non-combustible, stable to dry heat up to 125° and moist heat up to 50–60°. It decomposes at 135–150°.

Specific Gravity	1.64
Bulking Value	0.0735 gal/lb
Moisture Content	Less than 0.5 %
Moisture Vapor Permeability (g/cm ² /0.01 cm/hr at 21°)	0.2×10^{-4}
Tensile Strength	4200–5600 lb/sq in
Elongation	3–4 %
Modulus of Elasticity	1.47×10^5 lb/sq in
Film Hardness (Sward Hardness Index)	90 % of glass
Index of Refraction	1.554
Dielectric Strength	2300 v/mil
Dielectric Constant (1000 cycles—25°)	3.1
Power Factor (1000 cycles—25°)	0.0015–0.0030
Specific Surface Resistivity (ohms $\times 10^{-10}$)	2000
Water Absorption (24 hrs—80 % r.h.)	0.27 %

* Compiled from various literature of Hercules Powder Company.

Table 139. Properties of Chlorinated GR-S *

Chlorine content	53 %
Viscosity (20 % solution toluene)	0.50–20.0 poises
Solubility	Aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters of organic acids.
Compatibility (5 % or more)	Paraffin, chlorinated paraffins, tricresylphosphate, dibutyl phthalate, isobutyl linoleate.
Stability	Equal to chlorinated natural rubber.
Softening point	75–85°

Moisture vapor transmission on glassine:

Coating Weight lbs/ream	M. V. T. gms/sq m/24 hrs
3.3	114.7
5.6	70.4
10.5	49.9
Flexibility	Greater than chlorinated natural rubber
Specific gravity	1.36–1.39
Adhesion	Equal to chlorinated natural rubber
Tensile strength	5100 lbs/sq in
Elongation	18.7 %

Military uses of chlorinated rubber include sparkproof surface coatings for ordnance plants, flame-proofing compositions for tents and tarpaulins, adhesives for bonding rubber to metal, finishes for Army trucks, Navy paints, foundry core sprays, and tracer shells.

Since Pearl Harbor, much investigation has been made of the possibility of developing chlorinated derivatives of synthetic butadiene rubbers. Several materials of this type have appeared on the market to a limited extent. Numerous polymers have been studied from the point of view of chlorination. GR-S, for example, gives a chlorinated material having the characteristics listed in Table 139.

Polymerized isoprene is favored as a basic material for current chlorinated derivatives of this character. "Pliochlor," for example, produced from polyisoprene in experimental quantities by Goodyear exhibits the properties listed in Table 140.

Table 140. Properties of "Pliochlor" *

Color: White to cream	
Chlorine content: 60-70%	
Softening point: 94-108°	
Thermal stability at 120°	
Without stabilizer: 18 minutes	
A widely used chlorinated natural rubber: 3 minutes	
Light stability	
Weatherometer test: good	
Specific gravity: 1.48	
Iodine number: 0.24-0.53	
Viscosity range	
20% solution in toluene: 10-150 cps.	
Solubility:	
Soluble in:	
benzene	ethyl acetate
toluene	chloroform
xylene	carbon tetrachloride
"Solvesso" #1	chlorobenzene
methyl ethyl ketone	ethylene dichloride
Insoluble in:	
methanol	isobutyl alcohol
ethanol	aliphatic hydrocarbons
Compatibility:	
Compatible up to 50% or more with—	
chlorinated biphenyls	
dibutyl tartrate	
linseed oil	
tricresyl phosphate	
cumarone-indene resins	
diamyl naphthalene	
chlorinated paraffin	
triacetin	
dibutyl phthalate	
Film-forming qualities:	
Gives clear films from solution.	

* Manufacturers' data. The Goodyear Tire & Rubber Co., Inc.

Chlorinated rubber hydrochloride has been produced developmentally, but does not appear to have received much commercial recognition.

Oxidized Rubber

The oxidation of rubber is nominally one of its most serious weaknesses. Some work has been done, however, upon the production of semi-synthetic plastics by controlled oxidation. Most promising of such materials are the so-called "Rubbones," made by the action of air upon rubber containing cobalt linoleate in amounts of about 0.5 per cent. Oxidation can be carried out either by milling or by passage of air into a rubber solution. The products have been found suitable for paints and insulating varnishes and appear to be thermosetting in character. Commercial development of these materials, both in England where they were first developed and elsewhere, has lagged.

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Chapter 22

Cellulose Plastics

Cellulose

Introduction. Cellulose occupies a position of extreme importance in science and industry, as well as in life itself. Almost always associated with lignin and other substances, it is universally present in more or less fibrous form throughout the vegetable kingdom. Even coal deposits of the mineral world are attributable, in part, to cellulose from plants of distant ages, long buried in the soil.

Wood, for centuries used as fuel and as a material of construction, is largely cellulosic in nature. Among building materials it possesses the unique distinction of being perennially capable of renewal by wise cultivation along sound conservational lines. Striking developments in modern methods of treating wood have increased its versatility and utility for structural purposes far beyond the limits imposed by simple wood-working technique. Resin-bonded plywood, resin-impregnated high-strength paper laminates, compregnated wood, and moldable products developed by impregnation of wood with urea or urea-formaldehyde condensation products are typical examples of the increased utility of this natural product.

In paper of all sorts, wood and other natural cellulosic fibers have found utility for many centuries. Innumerable paper-making processes and special paper products contribute enormously to the necessities and luxuries of modern living. The wisdom of centuries, records of government, art of masters, documents of business, letters of lovers—all these things owe their preservation to the cellulosic matter upon which they are inscribed. And goods of all kinds are packed and shipped in board containers and paper cartons.

Molded wood pulp, sometimes combined with glue and other materials like clay or chalk, is fabricated into papier-mâché. Long known in the Orient, it was introduced into Europe during the 18th Century and is among the earliest of shaped organic plastics. It has retained a position of preeminence in the manufacture of myriad articles such as toys, paper pie plates, milliners' blocks, mirror and picture frames, and objets d'art.

Vulcanized fiber, another wood derivative, is widely used in shipping

drums and waste baskets, in electrical insulation, and in molded articles varying from prosaic faucet packings to artistic imitations of wood carvings applied as furniture decoration.

Rope made from cellulose in the form of hemp and sisal is indispensable to farming, shipping, and industry, and to a host of other fields of daily enterprise.

Cotton, king of crops, clothes mankind.

Flax yields fine linens, highly prized.

Bagasse, cornstalks, wheat straw, and even extracted licorice root, all high in cellulose, are made into light-weight insulation board and tile, such as "Celotex," "Maizewood," and "Maftex."

Cellulosic materials in various forms are indispensable fillers for many molded plastic products.

By chemical metamorphoses, cellulose is fabricated into a wide variety of vastly different articles now commonplace in daily life—from cellophane to rayon, from "Celluloid" to guncotton, from automobile lacquers to imitation leather. Even the field of surgery has been invaded by chemical derivatives of cellulose, for a newly developed form of oxidized cotton can be absorbed by the body and, soaked in thrombin, has been successfully used to stop bleeding during operations on the brain—subsequent removal being unnecessary.

It is beyond the scope of this volume to discuss most of these manifold materials. Only chemical modifications of cellulose will be mentioned in this chapter. Even treatment of this subject must be highly inadequate, for in no other field of the science and technology of plastics is the literature more replete with treatises and voluminous publications.

The Chemical Nature of Cellulose. Cellulose is a carbohydrate corresponding to the general empirical formula $[C_6(H_2O)_5]_x$. The value of x (the degree of polymerization) varies, depending upon the botanical source of the cellulose. Moreover, estimates of x for cellulose of any given origin differ widely from one observer to another, reported molecular weights ranging from 25,000 to 570,000.

Staudinger and his collaborators have obtained values shown in Table 141 for the degree of polymerization of various forms of cellulose.

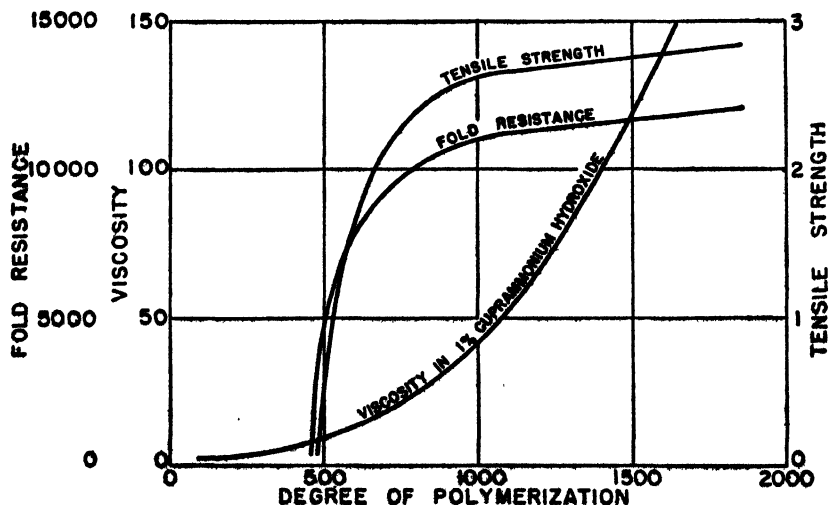
The degree of polymerization of cellulose and its derivatives has, for many years, been a bone of contention among chemists. The development of ultracentrifugal methods of analysis seems finally to have set the stamp of approval upon judicious use of viscometric methods of molecular weight determination. The extent of agreement now achieved between eminent authorities concerning the degree of polymerization of cellulosic substances is indicated in Table 142.

Table 141. Degree of Polymerization of Various Forms of Natural Cellulose ^{85,86}

Material	D. P.
Native cotton	2020
Cotton linters	1440
Ramie	2660
Baden flax	2420
Belgian flax	2390
Italian hemp	2300
Nettle	2280
Baden hemp	2200
German hemp	2200
Papyrus	2000
Manila	1990
Jute	1920
Willow (purified)	1710

Table 142. Extent of Agreement Between Various Investigators on the Degree of Polymerization of Cellulose Products

Material	Degree of Polymerization according to Staudinger ⁸⁶ (Viscometric)	Degree of Polymerization according to Kraemer ^{85, 86}	
		(Viscometric)	Sedimentation Equilibrium (Ultracentrifuge)
Native cellulose	2000-3000	3500	—
Cotton linters, purified	700-1400	1000-3000	890-1300
Wood pulp, purified	900-1500	600-1000	—
Regenerated cellulose, commercial	250-500	200-600	400-490
Dynamite nitrocellulose	1000-3000	3000-3500	—
Lacquer-type nitrocellulose	300-600	175-600	390-600
Cellulose acetate, commercial	200-350	175-360	190-380
Ethyl cellulose, commercial	200-500	—	540

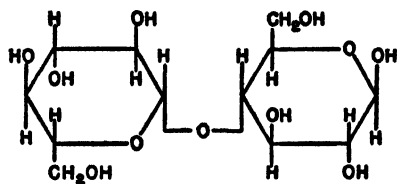
Figure 265. Relation of the degree of polymerization of cellulose to its viscosity in 1 per cent solution in cuprammonium hydroxide and to certain physical properties as determined on cotton fibers. (Staudinger ⁸⁷)

As the degree of polymerization of cellulose increases, its physical properties asymptotically approach maximum values. This fact is shown in Figure 265.

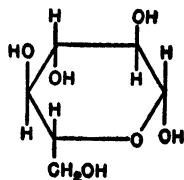
The same sort of trend is shown by cellulose derivatives, although the shape and location of the curves is not the same as with cellulose itself. This fact is of practical significance, for nearly optimum strength characteristics can be obtained in cellulosic derivatives whose degree of polymerization is sufficiently low to yield solutions of moderate viscosity so that they can be readily handled.

The constitution of cellulose remained an enigma for many years. Numerous formulas were proposed. None was altogether satisfactory. Although a multitude of researches aided in its elucidation, the greatest contribution to the solution of this knotty problem was made by the English chemist, Haworth, and his school.

Upon complete hydrolysis, cellulose yields glucose. Under special hydrolytic conditions, cellobiose,

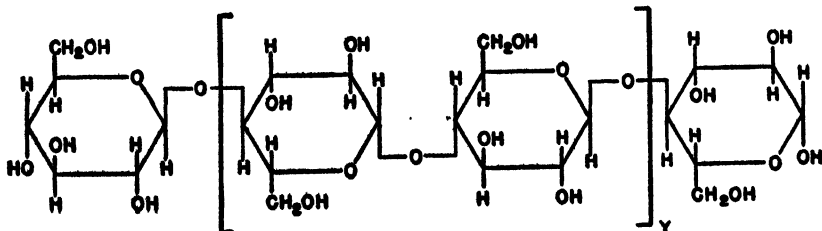


a disaccharide of β -glucose,



is obtained.

Cellulose is therefore considered to be a long, linear polymer of β -glucose in which the rings are united as in cellobiose; it is now represented by the following structural formula:



Y is equal to $\frac{x}{2} - 1$, where x is the degree of polymerization of the glucose units.

Cellulose is capable of undergoing many chemical reactions, only a few of which will be mentioned here. Of particular interest to plastics technology is the fact that its hydroxyl groups are alcoholic in nature and can therefore be esterified or etherified. Its esters, in turn, can be hydrolyzed, thus regenerating cellulose. In carrying out these various reactions, a certain amount of depolymerization is usually encountered, its extent depending upon the nature of the reagents and the reaction conditions. Molecular degradation may be excessive if care is not exercised. Although cellulose itself chars and decomposes without melting, most of its derivatives, because of their linear character, soften sufficiently below their decomposition points to permit molding by various methods. They are thermoplastic in character. Plasticizers are usually incorporated with these resins to facilitate molding or film formation and to improve their properties.

Alginic acid and deacetylated chitin probably possess formulas similar to that given above for cellulose. In alginic acid, the $-\text{CH}_2\text{OH}$ groups are replaced by carboxyl radicals. In deacetylated chitin, the amino group replaces the hydroxyl in position 2, *i.e.*, on the carbon atom adjacent to the pseudo-aldehydic group of the glucose units.

The Physical Structure of Cellulosic Fibers. The absolute specific gravity of cellulose is 1.50 to 1.55. Its apparent specific gravity is usually much less and is subject to wide variation, according to origin. Cellulose is anisotropic, exhibiting double refraction. Its index in the direction of the fiber is 1.599; that perpendicular to the fiber is reported as 1.532.

The arrangement of the molecules within cellulosic fibers has been the subject of a vast amount of research in which x-ray data have played a vital role. It is now generally held that cellulose is built up of bundles of long molecules, held together in more or less parallel alignment by inter-molecular secondary valence forces which exist largely because of the highly polar hydroxyl groups present in considerable number.

Two parallel molecules held together by secondary valence forces have been likened to a closed zipper. Bundles of cellulose molecules might, perhaps, be compared to a handful of parallelly aligned and slightly moistened spaghetti in which the adhesion between the sticky surfaces would represent the secondary cohesive forces between molecules. These simple mechanical analogies are, to be sure, crude, but they express the general idea of elongated submicroscopic structures of more or less crystal-

line character resulting from the parallel orientation of long cellulose molecules. The crystallites are called micelles.

The concept of the micellar theory and the term micelle, itself, were both proposed in 1858 by a botanist, C. von Nägeli, to explain the anisotropic behavior of cellulose long before anything was known of its chemical structure. Lacking experimental verification, interest in this theory waxed and waned by periods until x-ray examinations showed its fundamental tenets to be sound. The lower dimensional limits of these micelles appear to be 60 to 70 Ångstroms in width and 600 in length. (One Ångstrom unit is 10^{-8} cm.) If the molecular weight of native cellulose falls in the order of magnitude of 300,000, corresponding to a degree of polymerization of about 2000, then the chain length of a single molecule is approximately 10,000 Ångstrom units, which is several times the minimum micelle length just given. Hence, an individual molecule may traverse a number of micelles. Some of the molecules will terminate within these micelles, while others will begin therein, resulting in an interlocking of the molecular structures by means of submicroscopic crystallites in such a way that a single filament will more or less resemble a parallel assemblage of unbroken linear molecules running throughout its entire length.

In hemp and ramie, the micelles appear to be oriented parallel to the fiber axis. In cotton they are turned spirally around it; in wood pulp they are parallel to it at the center, but deviate to an almost perpendicular position near the surface. In regenerated cellulose, the micelles are not appreciably oriented with respect to each other; hence the strength of rayon is much lower than that of native cellulose unless mechanical work, such as stretching, is performed in order to bring about some degree of continuous molecular alignment.

The tensile strength of various forms of cellulose increases with the degree of orientation of the micelles, as shown in Table 143.

Table 143. Tensile Strength of Various Forms of Cellulose ²²

Material	Tensile Strength (lbs per sq in)	
	Dry	Wet
Ramie	132,000	153,000
Flax	119,000	125,000
Cotton	33,000-114,000	34,000-118,000
Highly oriented viscose	87,000	75,000
Viscose	26,000-55,000	12,000-27,000

Vulcanized Fiber

A special form of chemically treated cellulose has been manufactured for many years under the name vulcanized fiber. It is made from ab-

sorbent paper containing a high alpha-cellulose content, preferably derived from rags. Paper is soaked in a solution of zinc chloride, an intramolecular swelling agent, and the gelatinous, swollen sheets are then pressed and physically welded together into a compact whole. The product is subsequently washed for a long time, the zinc chloride being removed by osmosis. The washed material is then dried while subjected to elevated pressure.

Vulcanized fiber is available in sheets, rods, tubes, and special forms and is produced in standard red, black, and gray colors. Other shades are available upon demand. It can be easily machined and can be shaped in hydraulic presses or standard sheet-metal forming machines. Prior to more complicated shaping operations it should be moistened with water to soften it.

As would be expected from its cellulosic nature, it absorbs large amounts of water upon aqueous immersion. Physical properties of a representative commercial product are listed in Table 144.

Table 144. Physical Properties of "Spaulding" Vulcanized Fiber Sheets^a
($\frac{1}{8}$ inch thickness)

Density	1.15
Tensile strength, min.	
Crosswise	6,000 lbs/sq in
Lengthwise	8,000 lbs/sq in
Compressive strength, min.	
Flatwise	20,000 lbs/sq in
Water absorption, max.	
2 hrs	55%
24 hrs	65%
Hardness, Brinell	10-15
Dielectric strength, min.	150 volts/mil
Zinc chloride content, max.	0.2%
Ash content	3% (red only: 7%)

Based on N.E.M.A. Standards and A.S.T.M. Specification D-710.

Standards have been set by the National Electrical Manufacturers Association for minimum strength and electrical properties and maximum water absorption. Permissible zinc chloride content is 0.2 per cent or less.

Vulcanized fiber is available under many trade names, including "Armite," "Diamond" Fiber, "Fyberoid," "National" Fiber, "Peerless" Fiber, "Spaulding" Fiber, "Taylor" Fiber, "Vulcoid," and "Vulcot."

Vulcanized fiber is widely used as an electrical insulating material where water resistance is not required. Its mechanical properties adapt it to use in shipping containers, waste paper baskets and roving cans, light weight floor trucks, bobbin heads, gaskets, trunks, suitcases, industrial shields, abrasive disc backing, and numerous other industrial and consumer goods.

Cellulose Nitrate

History. The various milestones in the development of cellulose nitrate have been delineated in Chapter 2. The very considerable contribution made by this material to the plastics industry in general is there dwelt upon. "Celluloid," the first semi-synthetic plastic save vulcanized rubber, has been affectionately dubbed "The grand-daddy of 'em all!" Nitrocellulose has seen pioneer service in explosives, photographic film, molded plastics, artificial silk, artificial leather, leather and airplane dopes, lacquers, and safety glass. It has often opened virgin fields which other more stable plastics have ultimately usurped. But even though it has been continually pushed around by new-comers, it remains a time-honored and useful product which is still manufactured in large amounts today.

Chemistry of Cellulose Nitrate. The hydroxyl groups of the cellulose molecule can be esterified by nitric acid. The product, cellulose nitrate, is commonly but inaccurately called nitrocellulose. Sulfuric acid is used to facilitate reaction, probably because of its dehydrating effect. Complete nitration would lead to the triester in which all three hydroxyl groups of each glucose unit were converted. The nitrogen content of such a product would be 14.2. This completely nitrated ester, however, is unstable and is not manufactured commercially. Lower degrees of nitration are attained in which the nitro groups are distributed throughout the molecular structure of the cellulose, presumably according to the law of averages. Commercial products contain from 10.7 to 13.1 per cent nitrogen, their utility varying with the degree of nitration. A nitrogen content of 11.1 per cent corresponds to the dinitrate, *i.e.*, two nitrate groups per glucose unit.

The extent of nitration is largely a function of the amount of water present in the mixed acid. Table 145 shows this relationship where the weight ratio of sulfuric to nitric acid is held constant.

By plotting nitric acid, sulfuric acid, and water contents of the mixed acid on triangular coordinates, it is possible to define the area within which cellulose nitrate of a given nitrogen content will be produced. Such a diagram has been constructed by C. Trogus and is shown in Figure 266. The dotted area in this illustration represents the proportions of reactants which give rise to an unstable, readily hydrolyzable oxonium compound corresponding to the formula $(C_6H_{10}O_5 \cdot HNO_3)_x$. This substance, known after its discoverer as Knecht's compound, is not a true nitrate, but rather an addition product and its formation is avoided in commercial practice.

By fractional precipitation of solutions of industrial preparations of

Table 145. Influence of Water Content of Mixed Acid upon the Degree of Nitration of Cellulose²²

Nitration Mixture			Nitrate groups per glucose unit	Characteristics of Product	
H ₂ SO ₄ (%)	HNO ₃ (%)	H ₂ O (%)		Nitrogen content (%)	Solubility of product in ether-alcohol (% dissolved)
45.31	49.07	5.62	2.8	13.65	1.50
42.61	46.01	11.38	2.7	13.21	5.40
41.03	44.45	14.52	2.5	12.76	22.00
40.66	43.85	15.49	2.4	12.58	60.00
40.14	43.25	16.61	2.4	12.31	99.14
39.45	42.73	17.82	2.3	12.05	99.84
38.95	42.15	18.90	2.2	11.59	100.00
38.43	41.31	20.26	2.0	10.93	99.82
37.20	40.30	22.50	1.7	9.76	74.22
36.72	39.78	23.50	1.5	9.31	1.15
35.87	38.83	25.30	1.3	8.40	0.61
34.41	37.17	28.42	1.0	6.50	1.73

cellulose nitrate in acetone by means of heptane, it has been found possible to split them into many portions differing from each other in molecular weight—the least soluble possessing the highest degree of polymerization. Films prepared from any given fraction thus obtained resist repeated flexing better than unfractionated material of the same viscosity which, in turn, is superior to an equiviscous blend of high- and low-viscosity fractions. The improvement in properties attained by such fractionation is relatively slight, however, so that the minor advantages achieved do not justify its cost as an industrial procedure.

Molecular degradation occurs during nitration. By holding the temperature at 0° and prolonging the operation accordingly, however, it is possible to minimize molecular breakdown in this reaction better than in any other that cellulose undergoes. Further reduction in molecular weight of nitrocellulose can be brought about by heating with water under pressure after nitration is completed.

Manufacture of Cellulose Nitrate. Cotton linters are commonly used for nitration. Alpha-cellulose derived from purified wood pulp was also used in the manufacture of a certain amount of nitrocellulose during World War I. Recent developments have resulted in nitration of considerable quantities of high-grade bleached sulfite pulp.

Mechanical impurities are removed from cotton linters by digesting them for some six hours under pressure at about 160°, with sodium hydroxide of about 2 per cent concentration. Oil and mechanical impurities are thus removed. The alkali is then washed out and, for colorless grades of nitrocellulose, the linters are treated with a 2–3 per cent solution of bleaching powder at about 35°. Excess bleach is removed by sulfuric acid. The purified linters are washed, mechanically fluffed, and

dried to less than 1 per cent moisture content. Treatments with both alkali and bleach must be carefully controlled, depending upon the type of cellulose nitrate ultimately desired. Excessively vigorous conditions lead to formation of hydrocelluloses and oxycelluloses which are particularly undesirable in the manufacture of nitrocellulose for explosives inasmuch as their nitration products tend to decompose on standing. Sometimes, however, the cellulose is purposely degraded to some extent during these purification operations in order to reduce its viscosity where the final nitrated product is destined for lacquer use.

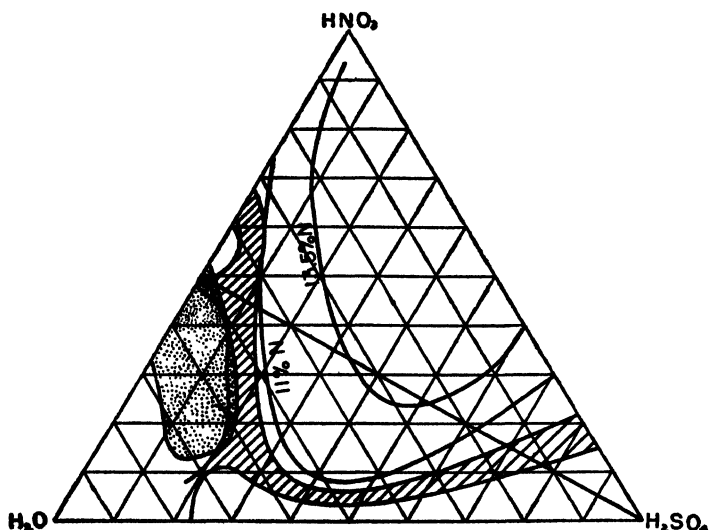


Figure 266. Triaxial diagram showing the nitration of cellulose by mixed acid. The dotted area indicates the field within which Knecht's compound is formed. The cross-hatched zone shows the area within which marked swelling of cellulosic fibers occurs. (Trogu⁹⁰)

The longer the various treatments and the higher the temperatures employed, the greater is the molecular breakdown. Occasionally recourse is had to digestion with sulfuric acid prior to nitration in order to lower the viscosity of the nitrocellulose subsequently produced.

Several different methods of nitration have been used industrially in this country and abroad. The pot, centrifugal, and Thomson displacement processes have been largely abandoned however, so that at the present time the so-called mechanical-dipper method is employed almost exclusively. Reaction is conducted in iron or stainless steel nitrators provided with two vertical, revolving paddles which operate against each other at a speed of about 60 rpm. The requisite amount of mixed

acid is run in and the paddles are started. The purified and dried cotton is then dumped in and quickly pulled beneath the surface by the arms of the agitators. Typical batches require from 32 to 40 pounds of purified linters. Somewhat larger amounts are now used in certain plants, but at best, only small batches can be nitrated at a time because of the difficulty of controlling the reaction. Approximately fifty times as much mixed acid, by weight, is employed. This large excess of acid is used in order to minimize the effects of changing concentration caused by removal of nitric acid and liberation of water during reaction. Where the approximate composition of the mixed acid corresponds to 25 per cent nitric acid, 55 per cent sulfuric acid, and the balance water, a product containing about 11.5 per cent nitrogen is obtained. If sulfuric and nitric acids are mixed in the ratio of 3:1, the nitrogen content of the product can be varied from 13.1 to 11.0 per cent by increasing the water from 7 to 20 per cent of the total. The temperature is usually held between 15 and 20°, although it may be raised as high as 55°. Reaction times range from 20 minutes to 1 hour.

When nitration is completed, the charge is dropped to a centrifuge on a lower floor where the spent acid is removed after whirling. Exposure of the wrung product to the atmosphere at this point occasionally results in fires. Spent acid is recirculated after fortification, while the nitrated cotton is forked loose from the centrifugals and immersed in a bowl filled with cold water. It is then washed to remove most of the acid and transferred to boiling tubs where unstable cellulose compounds, especially mixed nitrate-sulfates, are decomposed by means of live steam. Additional washes with water, alkaline solutions (especially aqueous sodium carbonate), and water are subsequently given the product to free it from all impurities. These operations are often referred to as stabilization. A bleaching operation is sometimes introduced before the final wash. Blending of different batches of cellulose nitrate is practiced in order to assure product uniformity.

The molecular weight of the nitrocellulose obtained by this series of operations is relatively high—from 70,000 to 150,000. The viscosity of its solutions is correspondingly high and therefore precludes its use in the dissolved state from all except specialty applications, although smokeless powder is manufactured from these straight nitration types.

For many years, the general utility of nitrocellulose in lacquers was limited by the high viscosity of its solutions. During the second decade of this century, methods were developed for reducing its molecular weight, resulting in consequent decrease in viscosity of its solutions. For the production of low-viscosity types of cellulose nitrate, several methods are available. It may be digested with water under heat and pressure;

it may be treated with various amines, such as pyridine; or its solutions in organic solvents may be degraded. The last two methods yield colored or unstable products. Hence, in commercial operations, the first one is the most practical. The way in which viscosity decreases upon aqueous digestion at 132° for varying lengths of time is indicated in Figure 267.

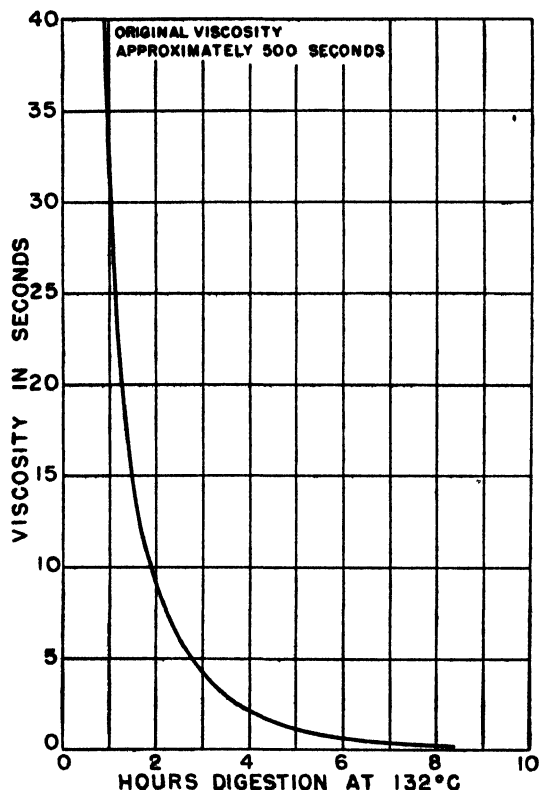


Figure 267. Relation between viscosity of cellulose nitrate and duration of treatment in the Milliken digester. (Original nitrogen content: 12.25 per cent. Nitrogen content at 15 sec viscosity: 12.17 per cent; at 4 sec: 12.15 per cent; at $\frac{1}{2}$ sec: 12.05 per cent; at $\frac{1}{4}$ sec: 12.00 per cent.) (Milliken⁷⁰)

Batch operations were universally practiced at first. Charges of nitrocellulose up to 2 tons and of water up to 30 tons were used. Slight decomposition occurs during digestion with evolution of nitrogen oxides. Probably because of entrainment of these gases in the nitrocellulose, dry spots sometimes occurred in the digesters, resulting in serious accidents. A vastly improved method of degradation has been introduced by Hercules Powder Company in the form of the Milliken digester to which the nitrocotton is pumped directly from the boiling tubs. This equipment consists of a 4000-foot, 4-inch chrome-steel coil heated by means of a steam jacket at the entrance end, insulated during most of its length,

and water-cooled near the exit. A 200-foot rise at the discharge end provides a hydrostatic back pressure against which the contents of the coil are pumped at 100 pounds per square inch. The water-nitrocellulose mix is passed through this digester at temperatures up to 160°. The total nitrocellulose content of the Milliken digester is 600 pounds, while the water in the system at any one time is about 6½ tons. Reduction of straight nitration grades of nitrocellulose to ½ second type can be accomplished in 25 minutes by passage through this installation. After digestion, subsequent washing and other treatments are carried out as in the case of straight nitration types.

Nitrocellulose is unsafe to store or ship in the dry state. It should be kept wet with alcohol. Instead of drying, therefore, the product obtained by settling or centrifuging and still wet with water is compressed under about 250 pounds per square inch. Denatured alcohol, or less often some other water-soluble alcohol such as isopropanol or butanol, is then pumped through the block to displace the remaining water. After complete dehydration, the pressure on the block is increased to 3000 lbs/sq in, whereby the alcohol content is decreased to about 30 per cent. The alcohol-wet block is then removed, broken up, and packed for shipment in air-tight containers to prevent evaporation. Throughout all these operations the cellulose retains its original physical form so that the final nitrated product resembles cotton waste in appearance, although it feels somewhat more harsh.

Grades of Cellulose Nitrate. Nitrocellulose is manufactured in a variety of grades, depending upon nitrogen content and viscosity, both of which determine its industrial applications. The four principal grades of cellulose nitrate are listed in Table 146 according to nitrogen content.

Table 146. Grades of Cellulose Nitrate According to Nitrogen Content

% Nitrogen	Characteristic Solubilities		Principal Applications
	Solvents	Non-Solvents	
10.7-11.2	Ethanol	Aliphatic hydrocarbons	Plastics, Alcohol-soluble lacquers
11.2-11.7	Methanol, ether-alcohol mixtures, ethyl acetate, acetone	Aliphatic hydrocarbons	Photographic film, Lacquers, (Rayon)
11.8-12.3	Amyl and butyl acetates, acetone, methanol, ether-alcohol mixtures	Ethanol, aliphatic hydrocarbons	Lacquers, Imitation leather
12.4-13.0	Acetone	Most other solvents	Gun cotton for smokeless powder and other high explosives

Nitrocellulose of any degree of nitration can be produced in any desired viscosity by controlled digestion. Relatively little nitrogen is lost

during this operation. The 11.8 to 12.3 per cent nitrogen grade, commonly known as pyroxylin or soluble cotton, is available in the widest range of viscosities, usually stated in terms of seconds as measured by the falling-ball viscometer. (This method of measurement has been developed by Hercules Powder Company, adopted in essence by the A.S.T.M., and is now generally accepted in the United States. The glass tube of the instrument is 355 mm long. Its internal diameter is 25.0 ± 0.5 mm. It is graduated with two marks placed 254.0 ± 0.8 mm apart, each line being about 50 mm from the corresponding end of the tube. The balls used are of steel, 7.938 ± 0.01 mm in diameter and weigh 2.0385 ± 0.007 gms, corresponding to an average 5/16 inch ball bearing. The temperature is held at $25.0 \pm 0.1^\circ$ and the time of fall is read to the nearest 1/5 sec. Time in seconds multiplied by 377 gives the viscosity in centipoises, except for the lowest grades. (The viscosity of water at 20° is 1.005 cps.) The nitrocellulose solution to be tested, corresponding to a lacquer containing 16 oz. of resin per gallon, is prepared as follows:

Dry nitrocellulose	12.2% by weight
Denatured alcohol	22.0
Ethyl acetate	17.5
Toluene	48.3

In making up this solution, the resin should first be wetted with alcohol and toluene before addition of ethyl acetate. Shaking facilitates solution.

In the cases of $\frac{1}{2}$ and $\frac{1}{4}$ second grades prepared according to this formula, the rate of fall is too great to yield an accurate measure of viscosity, so that longer falling times at higher concentrations are preferred. Recommended solutions are prepared by mixing $\frac{1}{2}$ or $\frac{1}{4}$ second grades with the above-listed solvents in the following respective proportions: 20%, 20%, 16%, 44% or 25%, 18.7%, 15.0%, 41.3%. Falling times are then 3 to 4 seconds or 4 to 5 seconds, according to type.)

It is probable that 600–1000 second nitrocellulose possesses a molecular weight of about 140,000; 30–40 second, about 68,000; and $\frac{1}{4}$ second, about 22,000.

General Properties of Cellulose Nitrate. Reference to Table 146 shows that the solubility characteristics of nitrocellulose vary according to nitrogen content. In general, lacquer solvents used with nitrocellulose for the formulation of industrial finishes can be divided into three principal groups: true solvents, latent solvents, and diluents. The most important true solvents in commercial use for the formulation of surface coatings include methyl, ethyl, isopropyl, butyl, and amyl ace-

tates, ethyl lactate, diethyl carbonate, anhydrous ethanol, mixtures of ethyl ether and ethyl alcohol, diacetone alcohol, acetone, methyl ethyl ketone, cyclohexanone, "Cellosolve," and various other glycol ethers and ether-esters. Latent solvents are liquids which are capable of dissolving nitrocellulose only where admixed with another solvent, either true or latent. Ethanol and ethyl ether are outstanding latent solvents

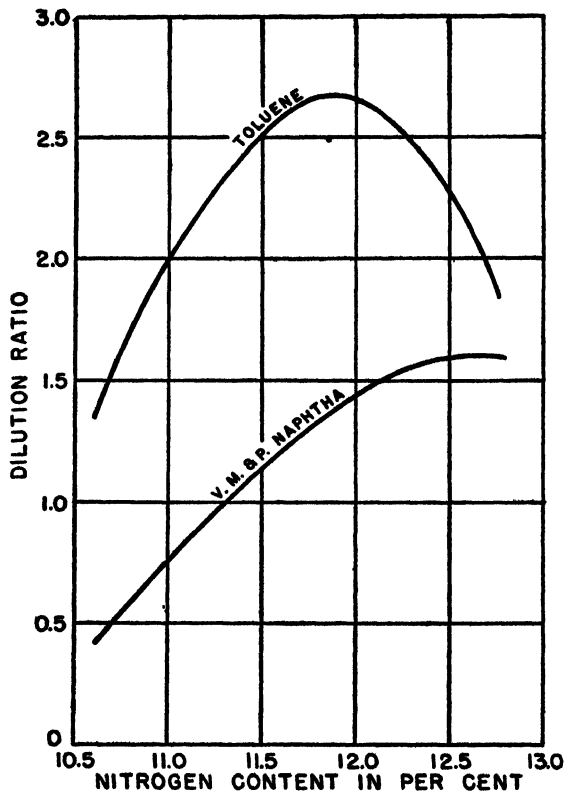


Figure 268. Relation between nitrogen content of $\frac{1}{2}$ sec nitrocellulose and tolerance of its butyl acetate solutions for specific diluents. (Dilution ratio is the volume of diluent divided by the volume of solvent in a 10 per cent nitrocellulose solution which contains maximum amount of diluent that can be tolerated. For method of determination, see Ref. 42.)

Courtesy Hercules Powder Co.⁴²

for pyroxylin. Alone, neither will dissolve this grade of nitrocellulose, but together they are an excellent solvent, widely used in collodion. Other latent solvents include C_3 to C_6 alcohols. A diluent is inactive as a solvent. Up to a certain maximum amount, defined in terms of dilution ratio with respect to a specific solvent, a diluent can be added to a solution of cellulose nitrate in a true solvent. Beyond this maximum, further addition of diluent causes precipitation of the resin. The most important diluents are benzene, toluene, and coal tar and petroleum naphthas. Variation of dilution ratio with nitrogen content of nitrocellulose is illustrated in Figure 268.

Plasticizers employed with nitrocellulose include camphor, castor oil, various drying oils, tricresyl phosphate, and dibutyl phthalate. Camphor is much the most important in molded plastics. Nitrocellulose is compatible with numerous natural resins, ester gum, and oil-modified alkyds, all of which are important in the formulation of surface coatings.

Nitrocellulose is readily flammable. The most highly nitrated types burn with great rapidity if ignited in the open. They explode upon detonation. The less nitrated types burn readily, but are non-explosive and cannot be detonated by percussion. The type used for solid plastics is least flammable.

Cellulose nitrate is relatively water resistant. It is not attacked by dilute acids. It is insoluble in aliphatic hydrocarbons and in carbon tetrachloride. Alkalies hydrolyze it slowly. Alkali and alkali earth hydrosulfides react with it quickly, regenerating the cellulose from which it came. This type of reaction was formerly utilized industrially in denitrating nitro-silk.

Purified cellulose nitrate is colorless, resembling cotton linters in appearance. It discolors and eventually decomposes under ultraviolet light. This effect used to be particularly noticeable in early safety glass manufactured with a nitrate interlayer. Deterioration is greatly reduced by combination of opaque pigments with this plastic, a fact which explains the contrasting longevity and excellent performance of automobile body lacquers based on this material.

It has been pointed out that cellulose nitrate is stabilized by removal of sulfate-nitrates and unstable derivatives of hydro- and oxy-celluloses during manufacture. Stability is determined by observing the time required for the vapors from a sample of resin, heated to 135°, to decolorize completely a methyl violet paper suspended above it. The resin can be further stabilized by incorporation of urea or diphenylamine therewith.

For detailed properties of cellulose nitrate plastic, see Tables 147 and 148.

Applications of Cellulose Nitrate. Nitrocellulose is utilized in four principal forms: as solid sheets, rods, and tubes, in film form, as a lacquer base, and as an explosive. Its earlier application in artificial silk has been abandoned.

The relation between nitrogen content and use has been cited in Table 146. The most highly nitrated esters, carefully purified and stabilized against liberation of nitrogen oxides by addition of a small amount of diphenylamine, are gelatinized by means of a suitable swelling agent, such as acetone, with or without the addition of nitroglycerin, and are pelleted or otherwise shaped into various forms of so-called

smokeless powder which may be dusted with graphite to prevent acquisition of static charges.

Cellulose nitrates of all lower commercial grades of nitration find use in the formulation of surface coatings for various purposes. The type most widely used is $\frac{1}{2}$ second pyroxylin of 11.8–12.3 per cent nitrogen

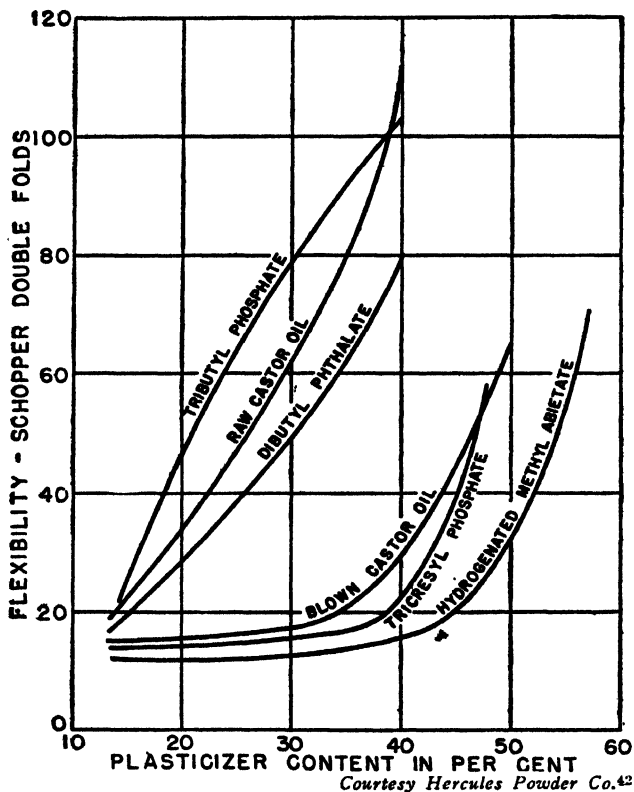


Figure 269. Relation between flexibility and plasticizer content of films based on $\frac{1}{2}$ second nitrocellulose and containing several different plasticizers. (Plasticizer content in per cent of total composition.)

content. Even where as much as 20 per cent of the lacquer consists of $\frac{1}{2}$ second pyroxylin, it will still be fluid enough for satisfactory application by spraying, brushing, or dipping. Still higher solids content can be obtained with lower-viscosity resins, but the films are somewhat more brittle. Automobile, furniture, and general lacquers of high solids content are made from low-viscosity grades. Fabric coatings are formulated with 8–10 second or higher types of resin which are also used in leather dopes, photographic film, and collodion.

In lacquer formulation, the nitrocellulose is dissolved in a true solvent,

such as butyl acetate, and a less expensive diluent is added, often a petroleum naphtha. The evaporation rate of the solvent and non-solvent should be similar so that solubility relationships will not be disturbed as the surface dries. To level out differences between various solvents and diluents which may be used together in a lacquer, such latent solvents as butyl alcohol are usually effective. They also smooth

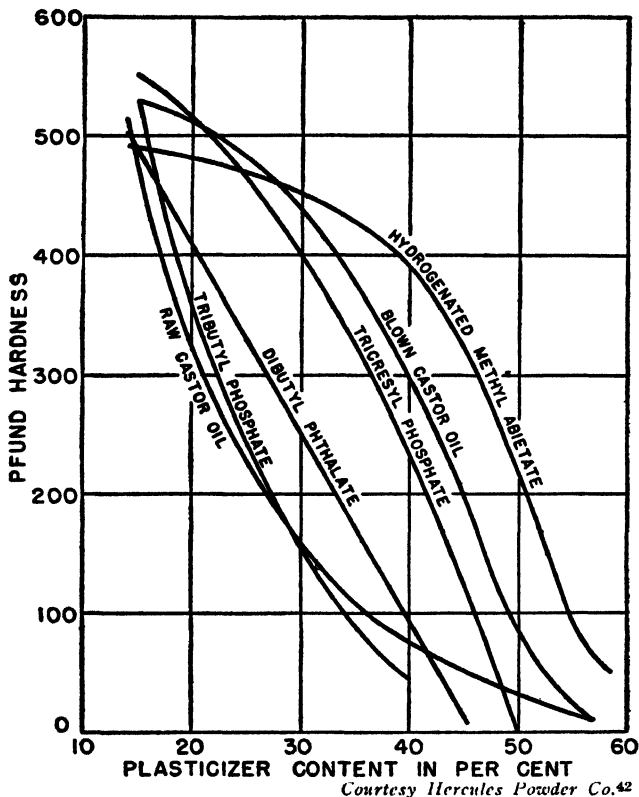


Figure 270. Relation between hardness and plasticizer content of films based on $\frac{1}{2}$ sec nitrocellulose and containing several different plasticizers. (Plasticizer content in per cent of total composition.)

out flow under the brush or upon spraying. Castor oil and other oils, tricresyl phosphate, and dibutyl phthalate are used as plasticizers in lacquers; camphor is not often employed because it is not retained permanently by thin films. Gloss is imparted by addition of various natural and synthetic resins, especially long drying oil-modified alkyds. For the dependence of flexibility and hardness of nitrocellulose films upon plasticizer content, see Figures 269 and 270.

Where denatured alcohol is used as a solvent, care should be taken to select a grade which contains no pyridine for the latter will cause degradation and decomposition of the film.

The uses of nitrocellulose lacquers and miscellaneous solutions are legion. Automobiles, display forms, floors, furniture, hardware, lighting fixtures, metal knobs, casings, and housings are all finished with cellulose nitrate coatings. Much military equipment is surfaced with nitrocellulose. Its solutions are employed in coating fabric of all kinds, as in the manufacture of imitation leather like "Fabrikoid," and in the production of window shades and patent leather.

Nitrocellulose solutions are also used in miscellaneous cements; combined with aluminum powder in "liquid solder"; used without pigments in transparent tarnish-proof metal coatings; combined with suitable resins in paper coatings. Other applications include moisture-proof coatings for "Cellophane," linoleum coatings, bronzing liquids, leather dopes, nail polish, and collodion.

Cellulose nitrate has been utilized in the manufacture of shaped plastics since the production of "Celluloid" by John Wesley Hyatt in 1868. The unique feature in the development of this plastic was discovery of the value of combining camphor with the nitrate. Despite the evolution of manifold plasticizers for other thermoplastics since the days of Hyatt, no other material is yet known that serves as well as camphor in cellulose nitrate sheets, rods, and tubes. To reduce flammability tricresyl phosphate may be used, but it is inferior to camphor except in lacquer formulation where the latter is not often employed because of volatility.

Contributing also to the success of Hyatt's "Celluloid" was the introduction of mechanical methods of plasticizing it without the use of large volumes of solvent. Refinements have been made since the early days of the industry, but the process still remains the same in principle. Cellulose nitrate, moistened with alcohol, is kneaded with camphor in a dough mixer. The fibrous character of the nitrate disappears during this operation and a uniform gelatinous mass is obtained which is filtered under hydraulic pressure and then transferred to large mixing rolls maintained at 150 to 175° F. Much of the alcohol used as solvent is evaporated at this point, while suitable dyes or pigments are uniformly incorporated if they have not been added previously. The milled plastic is then sheeted on the rolls into slabs which are piled on top of each other and pressed together hot. After this operation, sheets of any desired thickness are obtained by slicing from the compounded slab. To remove final traces of solvents, the sheets are aged by allowing them to stand for varying lengths of time, depending upon thickness, until all alcohol has evaporated. Warpage often occurs during this step, so that the final

operation is one of straightening, flattening, and polishing by means of steam-heated hydraulic presses.

Properties of plasticized cellulose nitrate plastics are exemplified by those of "Celluloid," limits of which are listed below.

Table 147. Physical Properties of "Celluloid" ¹⁰

Specific gravity	1.35-1.6
Tensile strength (lbs/sq in)	5000-10,000
Elongation (%)	10-40
Brinell hardness	
(kg/sq mm; 10 kg load; 2.5 mm ball)	5-11
Impact strength (ft lbs/in notch Charpy)	2-6
Thermal expansion (in/in/° C)	12 to 16 × 10 ⁻⁵
Thermal conductivity (cal/sec/sq cm/° C/cm)	3.1 to 5.1 × 10 ⁻⁴
Specific heat (cal/° C/gm)	0.34-0.38
Softening temp. (° F)	160-195
Ignition temp. (° F)	320-365
Dielectric strength (volts/mil)	600-1200
Dielectric constant (60 cycles)	6.7-7.3
Power factor (60 cycles)	0.06-0.15

The effect of various chemicals upon plasticized nitrocellulose is typified by the behavior of "Celluloid" upon immersion in the following reagents for seven days at 25°.

Table 148. Effects on Plasticized Cellulose Nitrate of Immersion for 7 Days in Chemical Reagents at 25° ¹⁰

Reagent	Effect on "Celluloid" after 7 Days
sulfuric acid, 30%	none
sulfuric acid, 3%	none
nitric acid, 10%	none
hydrochloric acid, 10%	none
acetic acid, 5%	none
oleic acid	none
sodium hydroxide, 10%	crazed
sodium hydroxide, 1%	crazed
ammonium hydroxide, 10%	crazed; discolored
sodium carbonate, 2%	none
sodium chloride, 10%	none
hydrogen peroxide, 3%	none
distilled water	none
ethyl alcohol, 50%	none
ethyl alcohol, 95%	dissolved
acetone	dissolved
ethyl acetate	dissolved
ethylene dichloride	partly dissolved
carbon tetrachloride	none
toluene	partly dissolved
gasoline	none

Plasticized cellulose nitrate is available in standard 20 × 50 inch sheets, from 0.005 to 1.00 inch thick. Sheets are produced in all colors, from transparent to opaque, and in a variety of special color designs

which can be developed, for example, by piling together differently colored slabs before pressing and slicing, then cutting across the grain after bonding. Mottled effects can be obtained by blocking alcohol-wet chopped material, instead of sheets.

Nitrate sheets can be blanked out, then molded to final shape at 250° F and 2000 lbs/sq in. Hollow articles can be readily blown, while other shapes are commonly drawn. These plastics are readily machined, polished, embossed, printed, engraved, and cemented together. In bonding parts of cellulose nitrate plastic, it is sufficient to moisten both pieces with a solvent like acetone, butyl acetate, or "Cellosolve" acetate. For bonding to other surfaces, nitrocellulose solutions containing a suitable plasticizer may be used.

Sheets of nitrate can be softened by means of aqueous methanol or acetone. The tough pliable product can then be stretched over various objects. Upon drying, it shrinks tightly about the enclosed article, yielding an attractive skin which can be cemented to the core around the edges. This process, using 80 per cent methanol, is employed in covering wooden shoe heels, hamper tops, and toilet seats.

Applications of cellulose nitrate sheet stock are legion. Buttons, buckles, ladies' handbag frames, piano keys, toys, combs, handles for knives, forks, hairbrushes, toothbrushes, and hand mirrors, eye shades, drawing instruments, spectacle frames, badges, marking tags, novelties, shoe lace tips, and corset rib covering are but a fraction of the myriad peacetime applications which have sprung from Hyatt's original search for a billiard ball. Military applications include powder containers, wad caps, shell closing caps, and numerous articles of civilian life which are indispensable in time of war for military purposes, such as drawing instruments.

In film form, cellulose nitrate is available in standard sizes and in continuous lengths up to 42 inches in width. Common gauges are 0.003 inch, 0.005, 0.0055, 0.0075, 0.00825, and 0.010. It is available in transparent colorless and colored forms. It is used as a photographic film base, in transparent envelopes and coverings, for artistic purposes such as drawing animated cartoons, and in certain containers for military explosives. An important industrial use for nitrocellulose sheeting is pipe line covering. Once used in safety glass, it has now been displaced by other types of plastics.

Plasticized nitrocellulose is also extruded in rods, tubes, and miscellaneous shapes. Extruded stock is a favorite for fountain pen and pencil barrels. Typewriter keys, umbrella handles, and dice are but a few among the many uses of these products.

Because of its inflammable nature and its tendency to decompose at

elevated temperatures, cellulose nitrate plastics are not used in either compression or injection molding operations.

Trade Names and Statistics. Cellulose nitrate is manufactured in a variety of nitrogen contents and viscosities by Hercules Powder Co., Inc., and E. I. du Pont de Nemours & Co., Inc. Plasticized cellulose nitrate in sheet, rod, and tube form is available under the trade names "Amerith," "Celluloid," "Nitron," "Nixonoid," and "Pyralin."

Nitrocellulose lacquers are available under many trade names and are very commonly admixed with other resins, especially oil-modified alkyds, in the preparation of industrial finishes. Two of the better known trade names are "Duco" and "Zapon," but a multitude of others are sold by paint and varnish houses.

In 1944, cellulose nitrate sold at 17 to 19 cents per pound, approximately 16,000,000 pounds being produced for plastics applications.

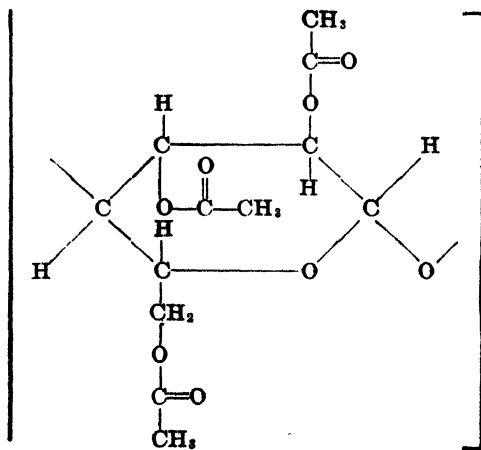
Cellulose Acetate

History. Like nitrocellulose, cellulose acetate has been intimately linked with the plastics industry for many years. Highlights in its historical evolution have already been sketched in Chapter 2. A French chemist of Alsatian origin, Paul Schutzenberger, was the first to prepare this semi-synthetic resin in 1865. The Britisher, C. F. Cross, together with his associates, attempted its development some thirty years later. Commercial utilization lagged, however, largely because of difficulties encountered in spinning filaments without the use of expensive and toxic chlorinated solvents and because of the inapplicability of the older dyestuffs and dyeing methods to artificial silks made therefrom. An American, G. W. Miles, was the first to overcome the former difficulty, but the latter was not surmounted until after World War I. The Dreyfus brothers established important factories in England and France for manufacture of airplane dope during that war. The armistice of 1918 forced re-direction of the products of their British Cellulose and Manufacturing Company into lanes of peaceful commerce as "Celanese." Toward the end of the nineteen twenties, cellulose acetate sheets, rods, and tubes first appeared, soon followed by molding powders. The latter grew in a spectacular manner as injection methods of molding thermoplastics developed early in the 'thirties. Evolution of improved methods of manufacturing acetic anhydride were reflected in decreased cost of this essential intermediate and permitted greater capitalization on the inherent advantages of both acetate silk and shaped acetate plastics. Recently, interest has been renewed in the earlier types of high-acetyl acetate for molded plastics because of its superior water resistance. Finally, when World War II broke out, high-strength acetate silk was in its

infancy. Its adaptability to the manufacture of parachute and balloon fabrics resulted in rapid development of "Fortisan" for military purposes.

Chemistry of Cellulose Acetate. The hydroxyl groups of cellulose are capable of yielding esters of numerous organic acids although the acids themselves are not sufficiently vigorous to bring about esterification. In the case of cellulose acetate, acetic anhydride is used as the active acetylating agent, being mixed with glacial acid. Moreover, catalysts such as sulfuric acid or zinc chloride must also be used. While these two chemicals are the most common catalysts, many others are equally effective. Phosphoric acid, perchloric acid, sulfur- and phosphorus-chlorides and oxychlorides, chloracetic acid, various sulfonic acids, and dimethyl sulfate are among those mentioned in the literature. All of these substances appear to exert more than a simple catalytic action. They probably form intermediate compounds with either acetic anhydride or cellulose, or with both. They seem to act, in part, by virtue of their dehydrating ability. Because they are intra-micellar swelling agents for cellulose, they loosen the physical intermolecular structure of the latter so that acetylating agents can reach and act upon the hydroxyl groups confined within the micelles.

There is an important difference between nitration and acetylation of cellulose. By control of the composition of the mixed acid used in nitrating, it is possible to vary the number of nitrate groups in the product. Under ordinary circumstances, however, it has not yet been found practicable to stop acetylation short of the completely esterified triacetate,



This material is often called primary cellulose acetate because it is the first product obtained by acetylation. Attempts to halt reaction at

an intermediate point yield only mixtures of unattacked cellulose and primary acetate. Miles' contribution lay in the discovery that, although acetylation could not be arrested short of the triacetate, yet it was possible to hydrolyze this ester partially to obtain a product having fewer than three acetate groups per glucose unit—usually about two. The primary acetate is soluble in chloroform, but insoluble in acetone. The reverse is true of the secondary acetate produced by partial hydrolysis.

It has been held in some quarters that the secondary acetate is not an incompletely acetylated cellulose, but rather a mixture of triacetate and regenerated cellulose. The evidence on this score, however, is far from convincing.

Acetylation of cellulose causes more degradation of the molecule than does nitration. Moreover, since acetic acid used in the reaction mixture is a solvent for the product, the original fibrous form of cellulose is not preserved. The molecular weight of cellulose acetate can be varied by changing the reaction conditions or by pretreating the cellulose with such reagents as formic acid, acetic acid, lactic acid, hydrochloric acid, oxidizing agents, or other substances. The degree of polymerization of commercial grades of cellulose acetate probably varies from about 175 to 360.

Manufacture of Cellulose Acetate. Cotton linters are the preferred source of cellulose for manufacture of the acetate. As in the case of nitrocellulose, it is essential to use a chemically purified grade of cotton which has been freed from oils and other mechanical impurities by cooking with dilute alkali and washing. Depending on the manufacturer, baled purified linters may or may not be first sent through a picker to loosen the fibers, then pretreated if necessary and carried to the acetylators. The viscosity of the cellulose acetate produced is determined not only by reaction conditions, but also by the details of purification and pretreatment of the cellulose used as raw material. It is essential to exercise careful control over drying of the linters. Too much moisture wastes acetic anhydride, makes temperature control more difficult, and lowers the viscosity of the product; if the cotton is too dry, it does not acetylate readily. Depending upon the manufacturer, moisture is usually held between 2 and 6 per cent.

Acetic acid and acetic anhydride, stored in aluminum tanks, are run through aluminum mains into a mixing vessel of the same metal. From there they are conveyed to the acetylator, often copper or bronze lined, where the requisite amount of sulfuric acid or other catalyst is added. The processed cotton is then slowly added to the acetylating mixture and stirred thoroughly for several hours, under carefully controlled temperature conditions, until sampling indicates reaction to be complete.

During a major portion of the acetylation, the reaction mixture is a thick paste, so that the acetylators are constructed in the form of heavy duty mixing devices of the ball-mill or dough-mixer type. Acetylation



Courtesy Tennessee Eastman Corp.

Figure 271. Cotton linters, acetic anhydride, acetic acid, and catalysts are reacted, with stirring, in this acetylator.



Courtesy Tennessee Eastman Corp.

Figure 272. Drawing cellulose acetate from the up-turned acetylator.

conditions vary according to the manufacturer, temperatures as high as 80° having been used, although much lower ones are customary. Where the product is used for the manufacture of acetate rayon, the lower the

temperature of reaction, the higher will be the tensile strength of the fibers. It is, however, of technical significance that over rather wide limits, yarn strength is but slightly affected by change in viscosity. Time-temperature relationships for a typical run are given in Figure 273 which also shows the point at which the mixture begins to acquire a dough-like character.

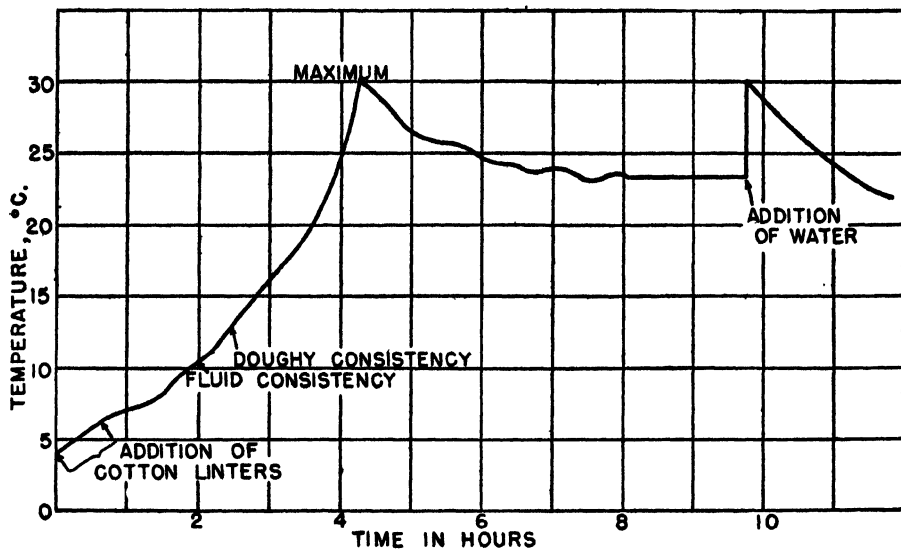


Figure 273. Course of typical acetylation of cellulose. (*Lipscomb*⁵⁹)

Depending upon the manufacturer, from a few hundred pounds to a ton of cotton linters may be acetylated at one time, control of reaction conditions being more easy than with nitration.

Some manufacturers add methylene chloride to the acetylating mixture because of its solvent power for the triacetate. Use of this solvent, handled in stainless steel equipment, assures homogeneity of solution with resultant uniformity of product.

The course of acetylation is followed toward the end of the operation by microscopic observation. Reaction is continued until the solution is relatively free from fibers. Complete reaction to remove all fibers is not always feasible, especially where a product of high viscosity is sought. Chemical examination is also made to ascertain the extent of consumption of acetic anhydride, uniformity of reaction, and viscosity of the product.

After acetylation is complete, a calculated amount of water, usually in the form of a 50-60 per cent aqueous acid solution, is added to the

reaction mixture. The water added is sufficient to cause hydrolysis, but insufficient to effect precipitation. The batch is then allowed to stand for a while at a carefully controlled temperature until analysis of samples and solubility determinations indicate that the original primary triacetate has hydrolyzed to a secondary acetate of the desired acetyl



Courtesy Tennessee Eastman Corp.

Figure 274. Cellulose acetate is hydrolyzed (saponified or ripened) in huge storage jars. Frequent tests insure uniformity in the finished products.

content. This process is known as saponification or ripening. In a typical saponification operation, water may be added to the extent of 22.5 per cent of the weight of the cellulose used and the mixture may stand for 65 to 75 hours at 21°. Saponification conditions, however, like those of acetylation, vary widely among manufacturers. Temperatures up to 70° are used, in which case the time required is shortened to only a few hours. Hydrolytic agents may also be added; hydrochloric acid or potassium nitrate are representative. Filtration is frequently carried out during or at the end of saponification, to remove fibers, and control is based mainly on viscosity measurements in domestic practice.

The theoretical acetyl content of cellulose triacetate, calculated as combined acetic acid, is 62.5 per cent. In practice, the primary acetate will contain only 62 per cent, or less—sometimes as low as 58 per cent. The difference is caused by the presence of a small amount of acid sulfate groups. The presence of these radicals in the finished product would lead to gradual decomposition on standing and charring upon heating at elevated temperatures. Hence, it is essential to hydrolyze whatever sulfate

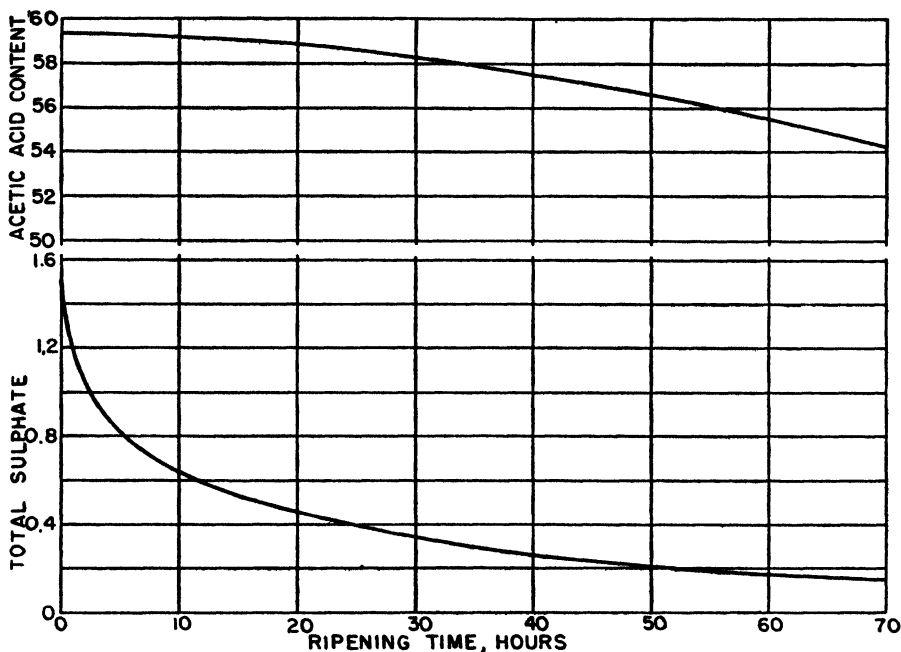


Figure 275. Change in combined acetic acid content and total sulfate of cellulose acetate during saponification. (Theoretical acetic acid content: triacetate: 62.5 per cent; diacetate: 48.8 per cent; monoacetate: 29.4 per cent.) (Plotted and adapted from data of Lipscomb ⁶⁹)

groups are present after acetylation. This operation is accomplished to a considerable extent during ripening. The change in both combined acetic acid and total sulfate as ripening progresses is shown in Figure 275.

After examination of the solubility of precipitated control samples in a series of solvent mixtures has shown saponification to have progressed far enough, precipitation of the secondary acetate is carried out by addition of a large excess of water, often with added sodium acetate to kill the sulfuric acid present. The secondary acetate so obtained may be stabilized by boiling with very dilute sulfuric acid (about 0.02 per cent) or it may be steamed with live steam to hydrolyze any residual

combined sulfate and improve stability, then washed, centrifuged, dried, and blended to insure uniformity. It is now ready for sale as such or for further processing.

Properties of Cellulose Acetate. In contrast to nitrocellulose, cellulose acetate is a light-stable, relatively nonflammable thermoplastic.

Its solubility characteristics depend upon the degree of acetylation. Primary acetate swells, but does not dissolve in acetone. It is soluble in



Courtesy Tennessee Eastman Corp.

Figure 276. Cellulose acetate compressed into manageable cakes which may eventually become photographic film, transparent wrapping material, molded plastic, or acetate yarns.

such chlorinated solvents as chloroform and methylene chloride. Secondary acetate is swelled by chloroform, but is insoluble in it. Acetone, methyl acetate, methyl ethyl ketone, nitromethane, dioxane, methyl "Cellosolve," and ethyl lactate dissolve the secondary acetate. Their efficiency as solvents, as reflected reciprocally in viscosity of solutions of a given concentration, decreases in the order given. Typical solvent pairs capable of dissolving secondary acetate are ethylene dichloride and ethyl alcohol (4:1), acetone and methanol (9:1), 1-nitropropane and ethanol (4:1). The effect of the nature of certain solvents upon viscosity is shown for Hercules' LL-1 cellulose acetate (55-56 per cent combined acetic acid, 2-4 sec viscosity) in Figure 277.

Within limits, both aromatic and aliphatic hydrocarbons can be used as diluents for cellulose acetate solutions. The tolerance of a given solution for aromatic hydrocarbons such as toluene is greater than that for aliphatic hydrocarbons.

Cellulose acetate plastics are resistant to dilute acids, gasoline, mineral and vegetable oils, and ethyl alcohol. Their resistance to water is not as good as that of other cellulose derivatives, a fact which has militated against applications where weathering is encountered.

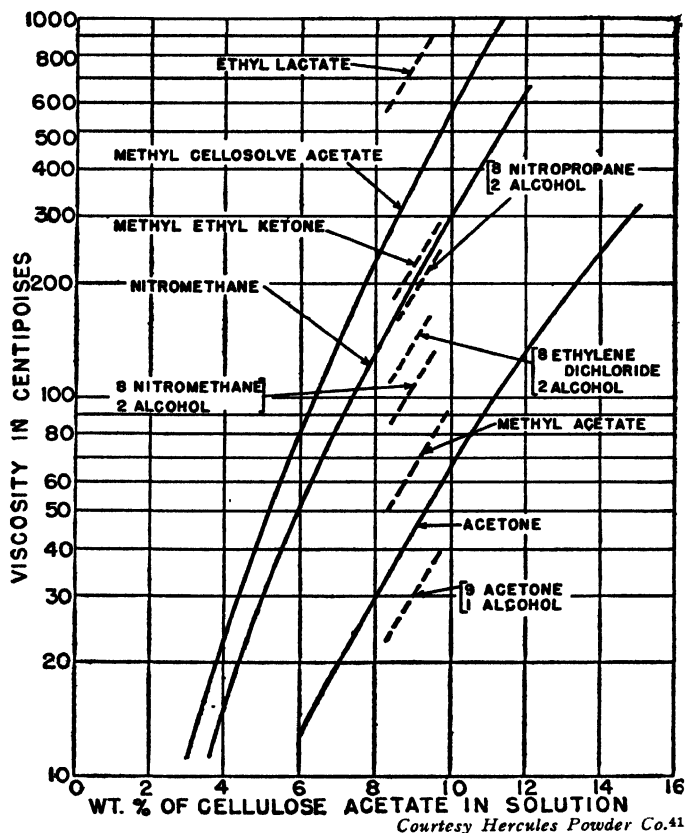


Figure 277. Effect of solvent on the viscosity of cellulose acetate solutions. (Hercules' LL-1 cellulose acetate; 55.4 per cent acetic acid, 2.4 sec viscosity, 228° softening point.)

Cellulose acetate does not possess wide compatibility with other resins, but shows limited compatibility with cellulose nitrate of low viscosity, with certain urea- and phenol-formaldehyde coating resins, with low-viscosity polyvinyl acetate, and with *p*-toluenesulfonamide-formaldehyde resins.

The number of plasticizers which can be used successfully with cellulose acetate is also restricted. Dimethyl and diethyl phthalates, methyl phthalyl ethyl glycolate, dimethoxyethyl phthalate, and triphenyl phosphate are often used, the last because of its fire-resisting properties,

Table 149. Common Plasticizers for Cellulose Acetate ¹¹

Plasticizer	Solvent Power	Water Resistance	Oil Proofness	Discoloration, Heat and Light	Remarks
Dimethyl phthalate	Excellent—52–60% acetic	Fair	Fair	Good	Toughens; volatile in lacquers; often used in plastics.
Diethyl phthalate	Good—52–58% acetic	Fair	Fair	Good	Toughens; volatile in lacquers; often used in plastics.
"Methox"—dimethyl "Cellosolve" phthalate	Good—52–58% acetic	Fair—Poor	Good	Good	Toughens; not volatile; toxic internally.
Diphenyl phthalate (solid)	Poor—compatible to 15% of C.A.	—	—	—	Alcohol-resisting; stiffener; makes high-melting films.
Dibutyl phthalate } Diamyl phthalate }	Poor—10% compatible with 53% acetic; 15%, 58% acetic	Fair	Fair	Good	Used with dimethyl phthalate to reduce warping and shrinking; may sweat.
"Santicizer" M-17—methyl phthalyl ethyl glycolate	Good—53–58% acetic	Good	Good	Good	Less volatile; for lacquer.
"Santicizer" E-15—ethyl phthalyl ethyl glycolate	Good—53–58% acetic	Good	Good	Good	Less volatile; for lacquer.
"Santicizer" 8— <i>p</i> -toluene sulfonamide	Good—52–59% acetic	Good	—	Fair	Lower melting point; blushes in humid conditions; hardens surfaces.
"Santicizer" 9—ethyl <i>p</i> -toluene sulfonamide (solid)	Good	Good	—	Fair	Lower melting point; blushes in humid conditions; hardens surfaces.
"Santicizer" 10—ethyl <i>p</i> -toluene sulfonate	Good	Fair	—	Poor	Lower melting point; blushes in humid conditions; hardens surfaces.
Triphenyl phosphate (solid)	Poor—58% acetic Fair—53% acetic	Good	Good	Fair—Good	Flameproof; stiffener, non-volatile; may be toxic.

Tributyl phosphate	Fair—53-58 %	Fair	Good	Good	Flame resisting; volatile.
Dibutyl tartrate	Good—52-58 % acetic	Poor	Good	Fair	Volatile.
Diamyl tartrate	Good—52-58 % acetic	Poor	Good	Fair	Volatile.
Camphor (solid)	Non-solvent compatible	Good	Fair	Fair	Stiffener; volatile; promotes surface hardness, compatibility of triphenyl phosphate and adhesion.
Triacetin	Excellent all acetics	Poor	Good	Good	Volatile; tends to hydrolyze; toughens.
Tripropionin	Fair—Good 52-58 % acetic	Fair	Good	Good	Less volatile than triacetin; toughens.
"KP-45"—diethylene glycol dipropionate	Good—52-58 % acetic	Poor	Good	Good	Volatile; toughens, softens plastics.
Acetyl triethyl citrate	Good	Fair	Good	Good	Less volatile than dimethyl phthalate; gives tough plastics.
Triethyl citrate	Good—52-58 % acetic	Poor	Good	Fair	More volatile.
Sucrose octa-acetate (solid)	Compatible	Fair	Fair	Fair	Stiffener; non-volatile; embrittles; improves adhesion.

Table 150. Properties of Hercules Cellulose Acetate of Various Degrees of Substitution ^a

<i>Physical Form:</i> Snow white, granular flakes					
<i>Color—Odor—Taste:</i> None					
<i>Melting Point:</i>					
% Acetic acid in ester	62	58	56	53	51
Capillary melting point, °C	270-290	260-280	240-280	235-245	250-270
Thermoplasticity or molding properties	None	Fair	Good	Very Good	Good
Density: At 25°, acetone soluble types = 1.4 (Bulking value = 0.085 gal/lb)					
<i>Refractive Index and Optical Properties:</i>					
Refractive index of films (Abbé) = 1.48					
Transmits light down to 2900 Å.U. (transmits all solar ultraviolet)					
Fluoresces slightly in ultraviolet, shows double refraction					
<i>Electrical Properties (Cellulose Acetate Films):</i>					
High internal and surface resistance—60 cycles, 20°					
Dielectric strength, volts/mil = 3000 (0.0012 inch film)					
Dielectric constant = 4.2-4.8					
% Power factor loss, 60 cycles = 1.8-2.2					
<i>Water Resistance:</i>					
Absorption of moisture by flake material					
% Acetic acid in ester	62	58	56	53	51
% Water absorbed, 100% R.H. at 25° (equilibrium)	3.5	7.0	8.6	15.1	16
Water permeability, K = gm/cm ² /cm/hr at 25° ($\times 10^{-4}$)	4.0	4.5	5.0	7.0	—
<i>Chemical Resistance:</i>					
Resists heat, weak acids, oils, greases, and fats. Not resistant to alkalis except in high acetylations. Lower acetylations (51-57%) soluble in acetone and lower ester solvents, materials above 60% soluble chiefly in mixtures of chlorinated solvents with alcohol.					

albeit it is not as efficient as the others. The behavior of a number of common plasticizers with cellulose acetate is given in Table 149.

Properties of unplasticized cellulose acetate of different degrees of acetylation are shown in Table 150.

Film characteristics of various grades of unplasticized cellulose acetate are given in Table 151.

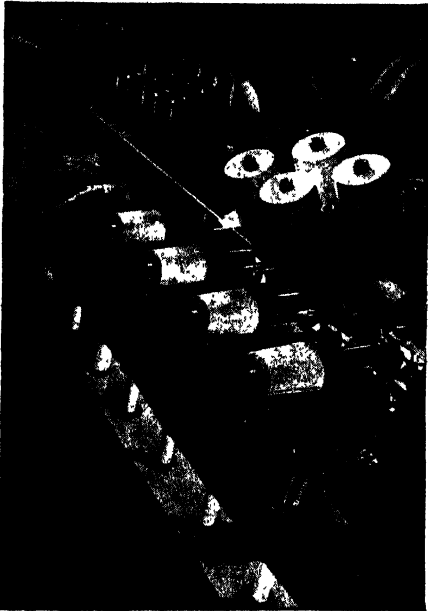


Figure 278. Acetate rayon being wound on cones from the pirns.

Courtesy E. I. du Pont de Nemours & Co.

The properties of plasticized cellulose acetate in film form and as molded plastics are given in the following section.

Commercial Forms and Applications of Cellulose Acetate. Cellulose acetate flake is utilized in the manufacture of acetate rayon, surface coatings, molding powders, sheet, rod and tube stock, and transparent films and foils. Expanded (cellular) cellulose acetate is a recent development.

In the production of acetate rayon, a secondary acetate containing 54-55 per cent combined acetic acid is employed. The flake is dissolved in acetone and the solution extruded through spinnerets into a warm current of air which evaporates the solvent so that filaments are produced without further treatment. Though wet spinning methods have been developed, they do not appear to be used commercially. Unlike nitro and viscose rayon, the acetate is not regenerated, except in the case of high-strength yarns. Both continuous filament and staple fibers are produced

Table 151. Film Characteristics—Hercules Cellulose Acetate ^a *
(Average Properties of Samples Tested)

Type	Symbol	% Acetic [†]	Viscosity sec	Tensile Strength kg/cm ²	% Elongation	Flexibility Schopper Double Folds	Shore Hardness	Softening Point, °C
P	PM-2	53.2	25	901	10.5	19	61	236
	PM-3	53.0	41	904	7.6	22	62	246
	PH-1	52.5	109	994	8.4	20	55	248
	PH-1	52.8	140	951	10.3	24	62	240
L	LL-1	55.4	2.4	677	3.3	7	45	228
	LM-1	54.5	44	924	10.6	24	58	237
	LH-1	54.2	75	950	7.7	26	60	249
	FM-3	56.1	22	866	5.0	20	50	239
F	FM-1	56.0	41	860	8.2	31	57	236
W	WH-1	57.9	92	970	7.0	15	62	240
T	TM	59.0	31	860	4.0	12	70	240

* Film tests were made on foils 0.003 inch thick, cast in the laboratory from solvent and dried with retarded evaporation under room conditions.

[†] Acetic content as determined by the Hercules method is reproducible within 0.2% acetic acid content and is a direct measure of acetylation. The method in brief is an alkaline saponification of a carefully prepared sample under standardized time and temperature.

in deniers * ranging from 1.5 to 4 and 1.5 to 20, respectively. The latter is used not only in textiles, but also in comforters and pillows to replace down. Continuous filament acetate yarn is manufactured in this country under such brands as "Acele," "Celanese," "Eastman" acetate, "Seraceta," and "Tubize," while staple fiber goes by the names of "Acele," "Celanese," "Seraceta-Fibro," and "Teca."

Acetate silk is resistant to laundering, an important factor in bringing it into popular favor during recent years.

Delustered filaments are manufactured by incorporation of titanium dioxide in the spinning solution. Because of its thermoplastic character, acetate silk lends itself admirably to special effects such as permanent pleats and moiré fabrics, fused edge ribbons, and tape for lining coat lapels. Special products include black filament colored before spinning, hollow filaments and more or less experimental bubble-filled filaments.

Acetate silk is dyed by means of water-insoluble dyes suspended in aqueous dispersion by means of various surface-active agents.

High-strength yarn is now produced from cellulose acetate under the trade name "Fortisan." This product is made by simultaneously hydrolyzing and stretching spun acetate by passage of the swollen thread under tension through a solution of an organic base at slightly elevated temperatures. Products made in this way may contain less than 1 per cent of acetic acid after hydrolysis. "Fortisan" is said to be as strong or stronger than other synthetic and natural yarns, strengths twice as great as that of natural silk being obtainable.

In 1941, American production of rayon yarns amounted to 451,204,000 pounds. Of this total, 163,745,000 pounds were of the cellulose acetate variety.

Cellulose acetate of 54–55 per cent acetic acid content is used in the formulation of a variety of surface coatings by solution in suitable solvents and combination with other resins, plasticizers, and pigments if desired. Viscosity grades range from 2 to 250 seconds, as measured by the time required for a 5/16 inch steel ball to fall through a distance of 10 inches in a 20 per cent solution of resin in a 9:1 mixture of acetone and ethyl alcohol contained in a tube one inch in diameter and held at 25°. Such lacquers are used for insulating purposes, for sealing bottles, for coating colored light bulbs, for coating textiles, papers, and metal foils, for preparing motion picture screens, and for numerous other purposes. High viscosity solutions are used as airplane dopes.

* Both monofilaments and composite threads are usually measured in terms of deniers. The denier of either a single filament or a thread is the weight in milligrams of nine meters thereof. The denier of a fiber of natural silk is about 1.3; that of wool may vary from about 1.2 to 30.



Figure 279. The first operation in making "Lumarith" is kneading cellulose acetate with sufficient solvent and plasticizer to facilitate handling.

Courtesy Celanese Plastics Corp.



Courtesy Celanese Plastics Corp.

Figure 280. Kneaded "Lumarith" is pressed through sieves. The filtered stock coming through the machine on the floor below is thus freed of impurities. (This is a combination of two photographs.)

Cellulose acetate molding powders have increased greatly in significance with the evolution of injection molding methods. The recent lack of availability of other plastics because of the military situation has also led to increased use of these materials, where possible, in consumer goods formerly made of phenolics. The usual type of cellulose acetate



Courtesy Celanese Plastics Corp.

Figure 281. Rolling "Lumarith" mass to disperse plasticizers and pigments evenly.



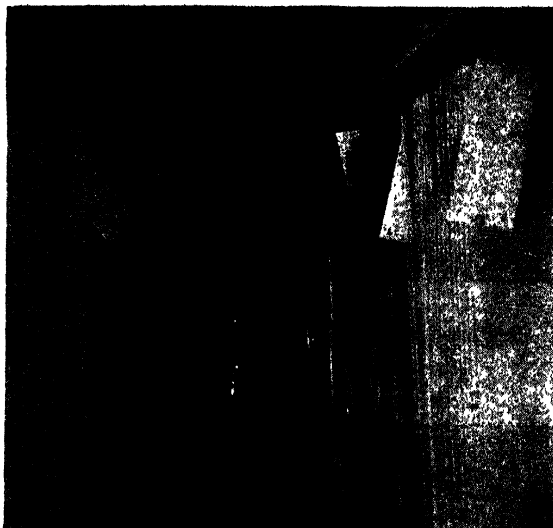
Courtesy Celanese Plastics Corp.

Figure 282. Removing rough "Lumarith" cake from pan.

employed in molding powders possesses a combined acetic acid content of 52-54 per cent. Powders are manufactured by incorporating plasticizers with flake acetate either with or without the aid of such solvents as acetone and alcohol. If solvents are used, a colloidal dough is prepared in a heavy duty kneading machine, then sheeted on warm rolls where the solvent is largely removed and coloring matter is incorporated.

The product is then chopped to granular form in a knife mill and dried. Heated Banbury mixers or hot rolls are employed for admixing the various molding powder ingredients in the absence of solvents.

Cellulose acetate molding powders are available in a wide range of transparent and opaque colors. Properties can be varied widely, depending upon the nature and amount of plasticizer used. Mottled colors are obtained by mixing differently colored powders. Such effects as particle size and sharpness of color outline in mottles can be varied by mixing differently colored powders of two or more degrees of flow.



Courtesy Celanese Plastics Corp.

Figure 283. "Lumarith" sheets hung in heated vaults for seasoning.

Cellulose acetate of a higher degree of acetylation than the regular plastics grade has been introduced for use in molding powders. Although somewhat more difficult to mold than the 52-54 per cent variety, this high acetyl acetate containing 56.5 to 58.5 per cent combined acetic acid still possesses satisfactory molding characteristics and shows better water- and heat-resistance than the standard grade.

The range of properties obtainable in variously compounded molding powders prepared with both regular and water-resistant grades of cellulose acetate is shown in Table 152. The approximate relationships between flow temperature of acetate molding powders and impact strength, modulus of elasticity, and heat distortion are shown graphically in Figure 284.

Table 152. Range of Properties of Commercial Molding Plastics ⁴¹

	Regular Plastics (P Type Hercules' Cellulose Acetate)		Water-resistant Plastics (W Type Hercules Cellulose Acetate)
	Transparents	Pigmented	Transparents
Density	1.27-1.32	1.37-1.56	1.27-1.32
Specific gravity, oz/cu in	0.73-0.76	0.79-0.90	0.73-0.76
Specific volume, cu in/lb	20.2-21.5	12.9-17.8	20.2-21.5
Strength tests:			
% Elongation at break	15-35	2.5-30	—
Tensile, lb/sq in	2800-5000	3000-4300	—
Compressive, lb/sq in	4000-12,000	11,000-16,000	—
Transverse, lb/sq in	6000-7000	6000-7000	5000-8000
Impact, Charpy ft lb/sq in	3.2-5.2	2.2-4.5	1.5-3.5
Izod ft lb/sq in	0.5-1.2	0.17-0.6	—
Hardness, Rockwell M	20 to 60	20 to 60	20 to 35
Thermal expansion, in/in/° C	1.56-1.64 × 10 ⁻⁴	1.02-1.5 × 10 ⁻⁴	1-1.5 × 10 ⁻⁴
(steel = 0.109-0.132 × 10 ⁻⁴)			
Thermal conductivity, cal/cm sq/° C/sec	5.4 × 10 ⁻⁴	5.3-8.7 × 10 ⁻⁴	5-9 × 10 ⁻⁴
Specific heat, gm cal/gm/° C	0.4-0.5	0.35-0.5	0.35-0.45
Refractive index, <i>n_D</i>	1.47-1.51	varies	1.47
Dielectric strength, 60 cycles, volts/mil, 60% R.H., 25° C	300-500	250-500	350-500
Dielectric constant at 550 kilo- cycles	4.3-4.6	4.7-4.9	—
Dielectric constant at 60 cycles	4-5.0	4-5.0	4.5-5.5
Power factor at 550 kilocycles	7.7-13.7%	6.8-15.3%	—
Power factor, 60 cycles, 60% R.H., 25° C	1.5-2.5%	—	1-2%
Molding pressure, lb/sq in			
Compression	2000-5000	2000-5000	2000-5000 (only soft powders compression mold)
Injection	10,000-20,000	10,000-20,000	10,000-20,000
Molding temperature, ° F			
Compression	275-285	300-310	320-350
Injection	335-365	360-390	380-440
Mold shrinkage, in/in, cold mold to finished cold article	0.0025-0.0045	—	—
Water absorption, % 96 hr im- mersion	1.4-2.0	1.4-2.0	0.95-1.2
Plastic warping in 100% R.H. 100° F atmosphere	Bad to slight, depending on formula		Slight to none, depending on formula

Cellulose acetate powders are usually molded by injection or extrusion. Large moldings can be produced by compression methods, provided the mold is cooled before removal of the piece. Powders are classified according to flow. Certain manufacturers list as many as six degrees of hardness (H_g to H), medium hard (MH), medium (M), medium soft

(MS), and as many as ten degrees of softness ($S-S_{10}$), depending upon formulation. Flow temperatures according to which these different grades are classified are determined by the Peakes-Rossi flow tester by the method of A.S.T.M. D569-40T. Each degree of flow differs from the next harder or softer one by three to five degrees Centigrade.

Hardest grades are used for compression molding of small objects. Intermediate grades are employed for injection molding and for compression molding of large areas. Soft varieties are utilized in extrusion.

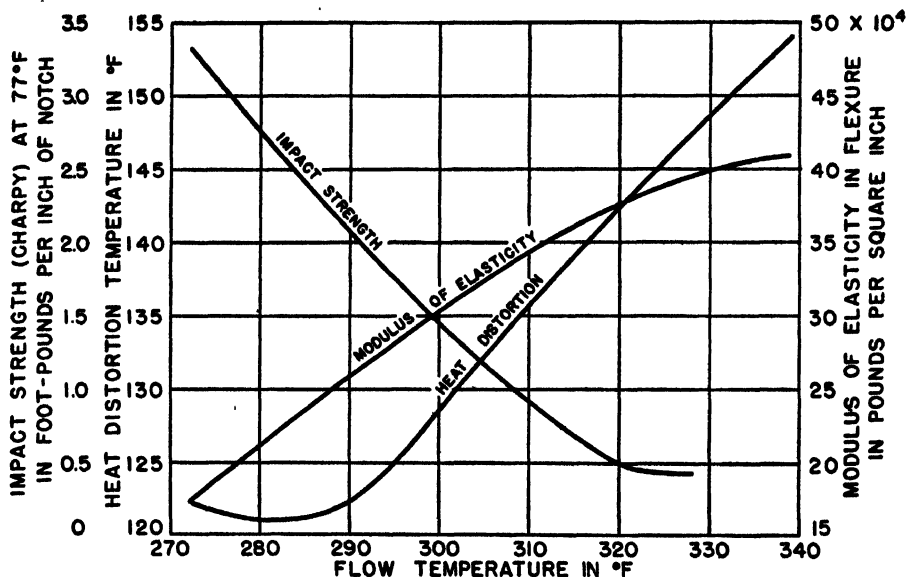


Figure 284. Relation of flow temperature to certain other properties of typical samples of injection molded cellulose acetate plastics. (Gloor³⁰)

Cellulose acetate molding powders are employed in fabrication of the greatest variety of articles where their thermoplastic nature is not detrimental to service and where extreme water resistance is not required. Some warpage is encountered in flows softer than MS. Cellulose acetate is not applicable where excellent dimensional stability is required or where the molded part will be exposed to temperatures in excess of 160° F. Typical uses include radio knobs, grilles, and housings, oil cups and transparent oil cans, electrical plugs, switchplates, and bases, buttons, buckles and costume jewelry, novelties such as combs, vanity cases, boudoir and desk accessories, telephone mouthpieces, automobile knobs, bezels, steering wheels and instrument panels, flashlight cases, tool handles, advertising models, garden hose nozzles, and extruded decorative trim.

Cellulose acetate readily lends itself to molding around inserts. Zinc die castings have been used as cores for injection molded automobile handles, for example. Another interesting application is to be found in acetate resins injection molded around glass lenses.

Military uses of cellulose acetate include transparent bullet coretips, gun sight lenses, gas mask flutter valves, airplane knobs, and injection molded gas mask lenses.

Cellulose acetate molding powders are sold under the trade names, "Lumarith," "Tenite" I, "Nixonite," "Fibestos," "Plastacele," and "Bakelite" cellulose acetate. In 1944, flake cellulose acetate was priced at 30-35 cents per pound. Molding powders, in plain colors ran from 34 to 48 cents per pound. About 57,000,000 pounds of acetate molding compounds were produced in 1944.

Plasticized sheets can be sliced from blocks prepared in much the same manner as cellulose nitrate. Sheets, rods, and tubes (approximately 8,000,000 pounds in 1944) sold under such trade names as "Lumarith," "Nixonite," "Fibestos" and "Plastacele" can be readily machined and formed. Blowing, printing, and cementing can be easily performed. Standard shapes and sizes are similar to those of nitrate. Typical uses are in telephone and radio parts, cable and wire insulation, lamp shades, light diffusers for fluorescent lamps, rigid transparent containers, machine guards, displays, pen and pencil barrels, drafting instruments, spectacle frames, industrial face shields and goggles, and identification tags. For a few years during the 'thirties, cellulose acetate largely displaced nitrate in the manufacture of safety glass because of improved light stability. It, in turn, has now been largely superseded in this application by polyvinyl butyral.

Important military applications of sheet acetate are to be found in transparent aircraft enclosures, especially for gliders and trainer planes, in windows of army barracks and blimps, in goggles and trainer gas mask eyepieces, in airplane fairleads, map cases, and printed charts, mileage scales, and computers of various kinds.

Films and foil less than 0.01 inch thick are cast from solution on highly polished moving surfaces, dried, and wound. They are used in photographic safety film and, in recent years, have gained an important place in transparent wrapping materials, envelopes, and bags. Before Pearl Harbor, films and foil found an important volume outlet in the fabrication of rigid transparent containers which added sales appeal to innumerable consumer goods. Vials and, to a limited extent, collapsible tubes are fabricated of acetate foil. Film is also used as electrical insulation on wire and coils and as spirally wound tubing. Typical properties of cast transparent films of cellulose acetate are given in Table 153.

Table 153. Properties of "Lumarith B," Cast Transparent Films of Cellulose Acetate Base¹⁰

Specific gravity	1.32-1.33			
Tensile strength, lbs/in ²	11,000-7,000			
Elongation, %	35-25			
Light transmission, %	92-88			
Heat shrinkage, %, 48 hrs at 140° F	0.1-0.25			
Humidity expansion, % (0% to 75% R.H. 24 hrs at each condition)	0.3-0.6			
Moisture absorption, % (24 hrs at 0% R.H. plus 48 hrs at 90% R.H.)	5-3.5			
<i>Electrical Properties</i>				
Gauge in 1/1000 in	3	5	7.5	10
Dielectric strength, volts/mil				
60 cycles, 50% R.H.	2440	2040	1650	1520
60 cycles, 24 hrs in water	1470	1220	840	690
Dielectric constant				
60 cycles, 60% R.H.	5.1	4.9	4.9	4.9
1 megacycle, 70% R.H.	3.6	3.9	3.8	3.7
Power factor				
60 cycles, 60% R.H.	0.016	0.016	0.016	0.016
1 megacycle, 70% R.H.	0.046	0.047	0.047	0.044
Volume resistivity, megohm-cm				
50% R.H.	26 × 10 ⁶	41 × 10 ⁶	78 × 10 ⁶	74 × 10 ⁶
24 hrs in water	32 × 10 ⁴	6 × 10 ⁴	12 × 10 ⁴	8 × 10 ⁴

Acetate foil is used for heat and pressure laminating to paper and fabric and for the protection and preservation of identification cards, and other records.

Film and foil are available under the trade names "Lumarith," "Plastacele," "Nixonite," "Vuelite," "Vue-Pak," and "Koda-Pak"

Acetate film laminated with cotton scrim or wire screening serves as a flexible glass substitute in hen houses, hot houses, military barracks and other explosion-resistant glazing, and ultraviolet transmissive hospital glazing. Products of this type are available under such trade names as "Lumapane," "Vimlite," and "Cel-O-Glass."

Cellular cellulose acetate, an expanded plastic free from plasticizer, designed for use in strong, light-weight cores for airplane floor panels, tail assemblies, and wing structures, and for application in luggage, prefabricated houses, and refrigerator insulation, is produced by du Pont in the form of extruded strips. It is available in four densities ranging from 4 to 9 lb/cu ft. It can be formed by heating to temperatures of 193-202°.

Mixed Cellulose Esters

Within the past decade extensive studies have been made of the characteristics of mixed esters of cellulose. Two types of such materials are

now available commercially, the acetate propionate, and acetate butyrate. Cellulose nitrate acetate has also been manufactured, but its production was stopped a few years ago to permit greater concentration upon the war effort on the part of its manufacturer. Each of these products can vary with respect to the total degree of esterification, the ratio of the two acyl radicals present, and the molecular weight as reflected in viscosity.

The acetate propionate is used primarily in surface coatings and in ex-

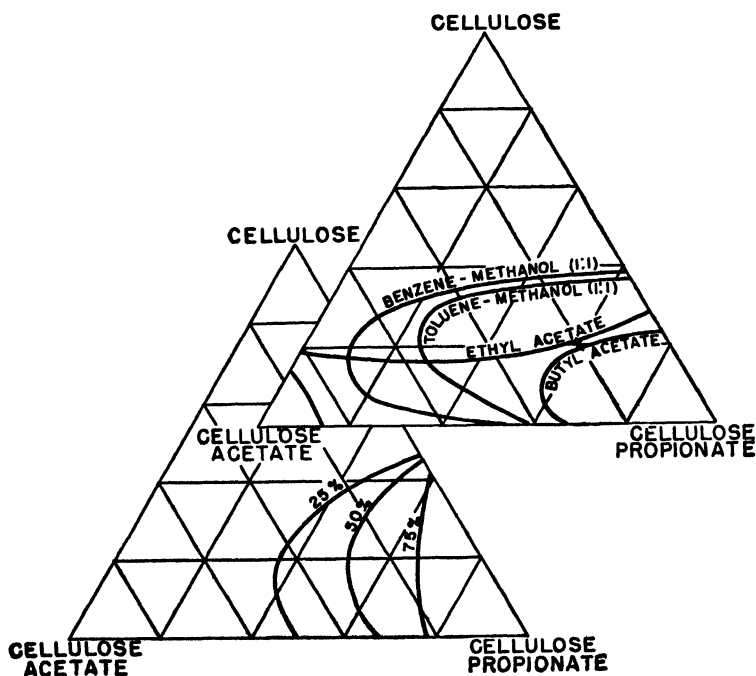


Figure 285. Solubility of cellulose acetate propionate compositions in organic solvents and compatibility of the same compositions with ester gum. (Ester gum indicated in lower chart as per cent by weight of cellulose ester.) (Fordyce, Salo, and Clarke²⁷)

truded filaments which are interwoven with cotton in the production of special fabrics for fused shirt collars. It is sold under the trade names of "Hercose" AP and "Eastman" acetate propionate. The acetate butyrate, sold under the trade names "Hercose" C and "Tenite" II, is used in both surface coatings and molding powders. Its adoption in molded and extruded plastics has been widespread.

Several undesirable characteristics of cellulose acetate such as moisture absorption, loss of plasticizer, and restricted compatibility with plas-

ticizers, solvents, and other resins, are improved by the partial replacement of acetyl groups by propionyl or butyryl radicals. Limits of solubility of these mixed esters and of their compatibility with various other resins have been established on triangular charts by Fordyce, Salo, and Clarke. Typical curves are shown in Figures 285 and 286.

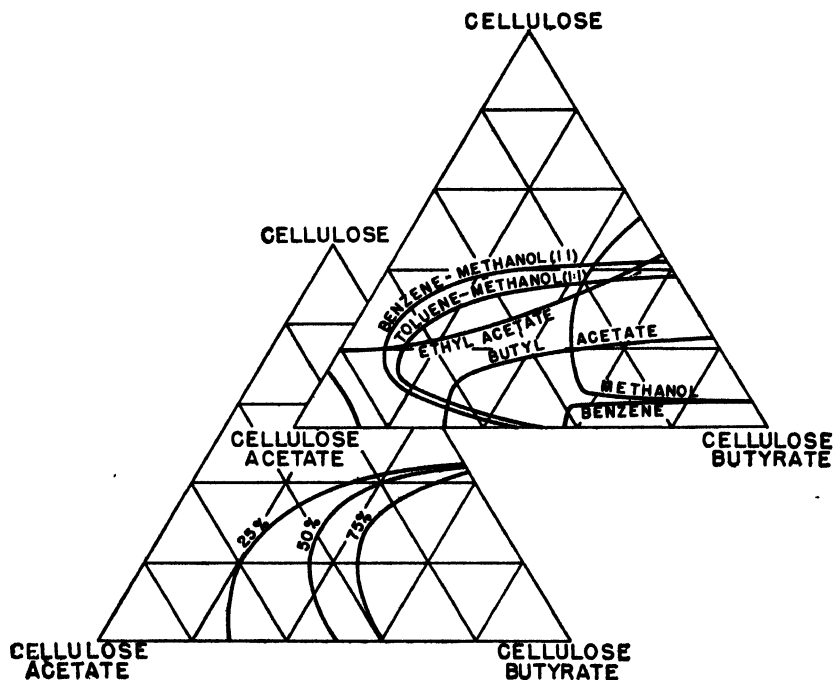


Figure 286. Solubility of cellulose acetate butyrate compositions in organic solvents and compatibility of the same compositions with ester gum. (Ester gum indicated in lower chart as per cent by weight of cellulose ester.) (Fordyce, Salo, and Clarke²⁷)

In Table 154 essential properties of "Hercose" AP, a lacquer-type resin containing about 31 per cent propionyl and 15 per cent acetyl, and of "Hercose" C, another lacquer-type resin containing 14–18 per cent butyryl and 32–36 per cent acetyl, are contrasted with those of nitrocellulose and cellulose acetate.

Cellulose acetate butyrate containing from 35 to 40 per cent butyryl is especially suitable for molding powders. "Tenite" II possesses about 13 per cent acetyl and 37 per cent butyryl. Cellulose acetate butyrate shows better weather resistance than cellulose acetate, partly because of lower water absorption, partly because of better compatibility with highly water resistant and non-volatile plasticizers, and partly because

Table 154. Comparison of Certain Properties of Unplasticized Films of Various Cellulose Derivatives⁴⁰

	"Hercose" C	Nitro- cellulose	Cellulose Acetate	"Hercose" AP
Moisture Permeability (gm H ₂ O/cm/cm ² /hr at 22° satu- rated air) $\times 10^{-3}$	4.0-5.0	2.4	6.0-8.0	4.1
Moisture Absorption, % (at 85% R.H., 22°)	3.0-3.3	3.1	8.0	3.2 (25°)
Tensile Strength: Breaking load— kg/cm ² (22° C, 60% R.H., 45 kg/ cm ² /min loading rate) *	400-550	600-800	500-600	500-530
Breaking Elongation	3.5-4.0%	4-6%	2-4%	7-11%

of superior retention of larger amounts of plasticizers as illustrated in Figure 287.

Table 155 compares the physical properties of the acetate and acetate butyrate where plasticized with the same materials. Incidentally, these

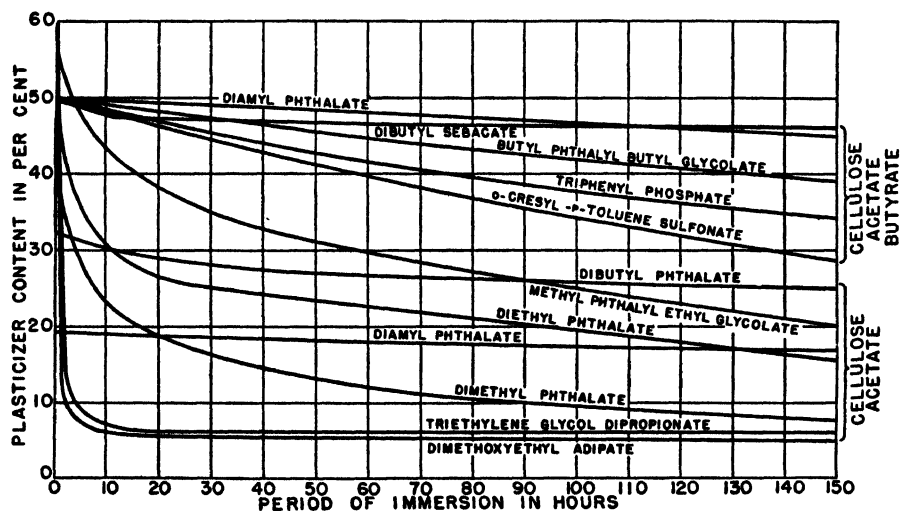


Figure 287. Comparative retention of plasticizers in cellulose acetate and cellulose acetate butyrate (37 per cent butyryl, 13 per cent acetyl) films immersed in water at 40°. (Adapted from Fordyce and Meyer²⁶)

resins are not compatible with each other and should never be mixed.

The relationship between flow temperature and physical properties of a typical injection molding formula of "Tenite" II is shown in Table 156.

In molded applications, cellulose acetate butyrate is employed much as cellulose acetate. Typical military uses include molded bayonet scab-

Table 155. Comparison of Physical Properties of Plastics Composed of Cellulose Acetate (38.5 Per Cent Acetyl) and Cellulose Acetate Butyrate (37 Per Cent Acetyl, 13 Per Cent Acetyl) with Various Plasticizers ^a

Parts Plasticizer per 100 parts base	Dimethyl Phthalate		Diethyl Phthalate		Dimethoxyethyl Phthalate	
	Cellulose Acetate	Cellulose Acetate Butyrate	Cellulose Acetate	Cellulose Acetate Butyrate	Cellulose Acetate	Cellulose Acetate Butyrate
Flow Temp, ° F	37.8	30.0	22.6	15.8	11.0	6.3
% Elongation	266	285	307	266	285	307
Tensile Strength, lb./sq in	8.0	6.5	5.0	23.8	22.7	21.8
Flexural Strength, lb./sq in	6,630	8,100	9,930	4690	5520	6,540
Rockwell Hardness M	11.140	14.200	17.000	7840	9240	10,950
% Water Absorption (48 hr)	79.5	90.5	101.1	72.4	80.1	86.4
% leaching (48 hr)	2.13	2.47	3.24	1.45	1.58	1.68
% loss in wt. (1 wk. at 150° F)	0.58	0.52	0.45	0.41	0.29	0.22
% shrinkage (1 wk. at 150° F)	2.40	0.86	0.53	1.06	0.60	0.46
	1.38	0.11	0.09	0.89	0.48	0.19
				3.02	1.53	0.70
				0.33	0.27	0.13
				0.29	0.21	0.17
				0.13	0.13	0.11
				0.09		

Table 156. "Tenite" II—Formula, 200^{ss}
(Bold face figures represent the critical limits)

Property	Temp	R.H.	H ₁		H ₂		MH		MS		S ₂		S ₄	
	° F	%	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Flow Temperature, ° F	—	—	323	341	305	323	291	309	277	295	263	281	251	269
Specific Gravity	77	50	1.23	1.25	1.22	1.24	1.21	1.23	1.21	1.23	1.21	1.23	1.21	1.23
Rockwell Hardness	77	50	R112	R118	R109	R115	R100	R111	R88	R108	R74	R100	R58	R88
Elongation, %	77	50	40	50	44	54	50	61	53	66	58	71	63	76
Load Impact Strength, ft.-lbs/in of molded notch	—	—	0.3	0.5	0.4	0.6	0.4	0.6	0.4	0.6	0.5	0.7	0.5	0.7
	77	50	0.5	1.0	0.7	1.4	1.0	2.2	1.3	3.0	1.9	3.9	2.6	4.8
Tensile Strength, psi	77	50	5,600	6,600	5,000	6,000	4,300	5,300	3,700	4,900	3,200	4,300	2,600	3,700
	160	—	3,500	5,000	2,800	4,000	2,000	3,200	1,500	2,700	1,000	2,000	750	1,500
Flexural Strength, psi	77	50	9,800	11,900	8,700	10,500	7,100	9,200	5,700	8,400	4,600	7,100	3,500	5,700
	160	—	6,600	8,800	5,500	7,400	4,000	6,100	2,800	5,200	1,900	4,000	1,000	2,800
Modulus of Elasticity, psi × 10 ⁴	77	50	1.71	1.98	1.54	1.80	1.32	1.62	1.10	1.50	0.91	1.32	0.71	1.10
	160	—	1.21	1.46	1.04	1.30	0.82	1.12	0.62	1.00	0.42	0.82	0.24	0.62
Distortion under Heat, ° F	—	—	155	190	145	170	130	150	120	140	115	130	110	120
Deformation under Load, % (Cold Flow)	122	—	1.3	7.9	3.1	16.0	7.9	32.3	13.6	39.0	23.9	43.5	36.5	47.2
Water Absorption (24 hours immersion)														
Total—%	77	—	1.6	2.1	1.5	1.8	1.4	1.6	1.2	1.5	1.2	1.4	1.0	1.3
Soluble Matter Lost, %	77	—	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1
Accelerated Aging, 72 Hours Weight Lost, %	180	—	<0.1	0.4	0.2	0.9	0.6	1.5	1.0	2.1	1.5	2.6	2.1	3.2

Formula 200 has high flexural and tensile strengths, modulus of elasticity and elongation, and low water absorption and soluble matter lost on immersion. The flow most used is MS. Applications: adding machine keys, tail lamp lenses.

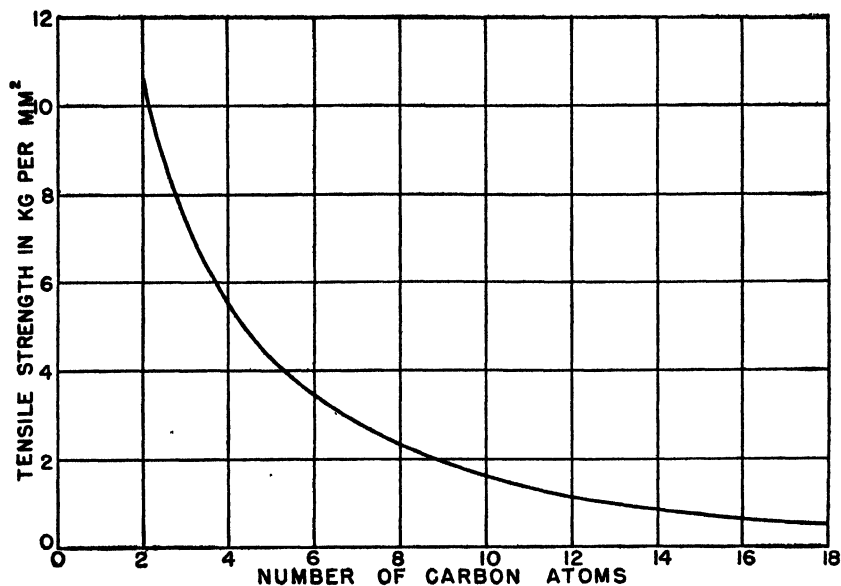


Figure 288. Tensile strength of sheets of cellulose triesters as a function of the number of carbon atoms in the esterifying acid. (Sheppard and Newsome⁸⁵, after Hagedorn and Moeller⁸²)

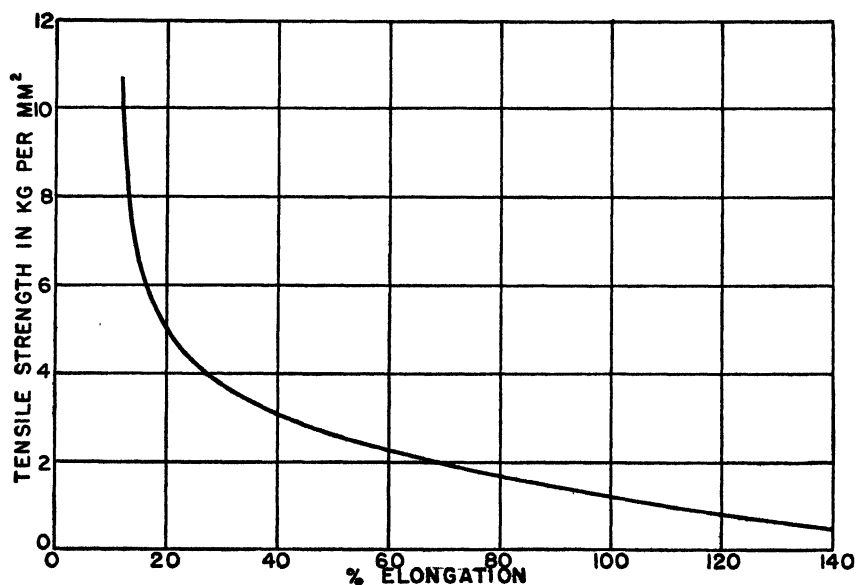


Figure 289. Tensile strength of sheets of cellulose triesters vs. elongation at the breaking point. (Sheppard and Newsome⁸⁵, after Hagedorn and Moeller⁸²)

bards, ammunition rollers, instrument dials, and blackout lenses for trucks.

Unique uses of extruded cellulose acetate butyrate have been developed in brilliant monofilaments woven into fabrics and lace for ladies' hand-

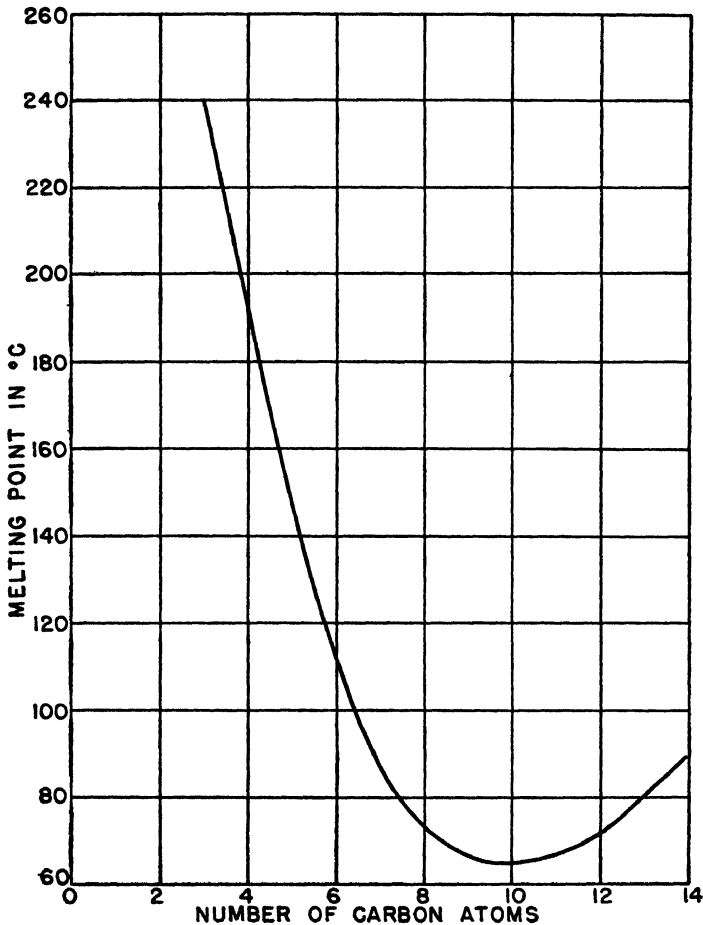


Figure 290. Melting point of cellulose triesters as a function of the number of carbon atoms in the esterifying acid. (Sheppard and Newsome⁸⁵)

bags, millinery, and decorative ornaments; in flat strips which have been interwoven for use in furniture upholstery; and in extruded transparent tubing.

In 1944, cellulose acetate butyrate molding powders, in plain colors, were priced at 35 to 50 cents per pound.

Higher Esters of Cellulose

The latest new-comer to the ranks of moldable cellulose plastics is the propionate which is now manufactured from propionic acid derived from petroleum. The amount of plasticizer used in cellulose propionate formu-

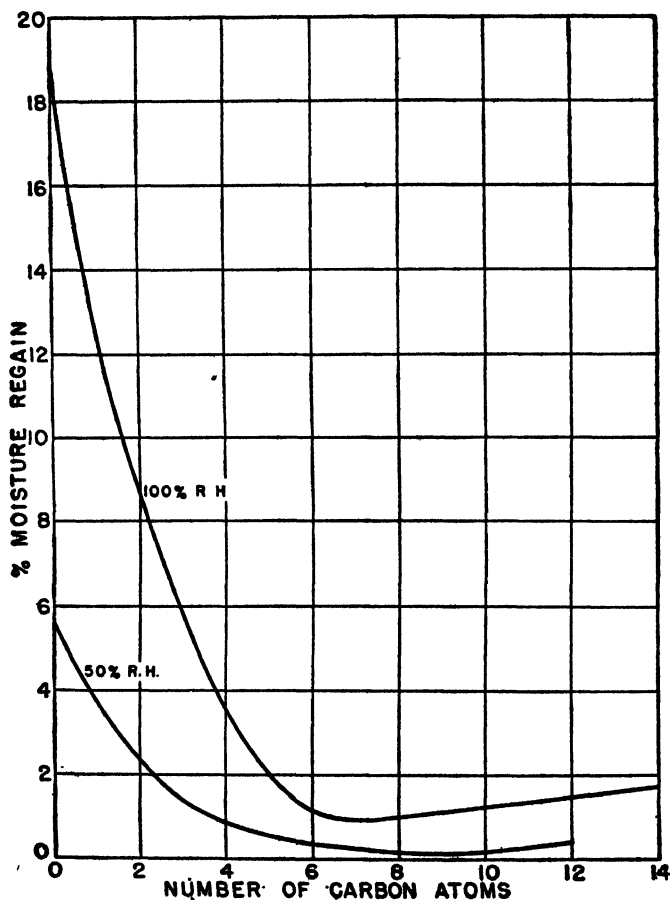


Figure 291. Relation between moisture regain at 25° of cellulose triesters, dried by evacuation at room temperature, and the number of carbon atoms in the esterifying acid. (Sheppard and Newsome⁸⁵)

lations is less than half the quantity required for cellulose acetate compositions of similar flexural strength. Characteristics of cellulose propionate plastic, available under the name "Forticel," have been described by R. H. Ball, *Modern Plastics*, 23, No. 4, 118 (Dec. 1945).

Although not presently used in commercial plastics, higher esters of

cellulose have been investigated to some extent. The relationships between tensile strength, elongation, and length of the fatty acid group in triesters prepared by action of the corresponding acid chloride upon cellulose in the presence of pyridine is shown in Figures 288 and 289.

Figures 290 and 291 show similar relationships between structure, softening point, and moisture regain.

Cellulose Ethers

General Principles. The hydroxyl groups of cellulose are capable of etherification as well as esterification. The most important general purpose commercial ether is ethyl cellulose. Methyl cellulose is produced in much smaller volume for special purposes. Benzyl cellulose has been made in developmental amounts, but has not attained much recognition. Hydroxyethyl cellulose is manufactured in limited quantities for textile treating applications. Carboxymethyl cellulose, otherwise known as cellulose glycolic acid, is available for similar purposes, while the surface layers of fibers in cotton fabrics may undergo partial conversion to stearoxymethyl cellulose during the so-called "Zelan" treatment for water-repellence. Numerous other ethers and even mixed ether esters have been made experimentally, but are not manufactured at present.

The general method used to produce ethyl, methyl, benzyl, and sometimes hydroxyethyl cellulose is the same. It involves preliminary digestion of purified cellulose, from either cotton linters or wood pulp, with concentrated sodium hydroxide solution—usually in the order of 50 per cent or higher. Conversion to so-called alkali cellulose or soda cellulose occurs and excess water and sodium hydroxide are expelled by pressing or centrifuging. The chemical nature of alkali cellulose has not yet been elucidated. It may be that some sort of addition compound is formed. Whatever the explanation, this product can enter into reaction with alkyl halides or sulfates in the sense of the Williamson synthesis, with elimination of the corresponding inorganic salt and formation of cellulose ethers. An excess of sodium hydroxide is always present; hence some hydrolysis of the alkylating agent to the corresponding alcohol occurs. The by-product alcohol so formed may, in turn, react with some halide to yield a dialkyl ether, especially in the presence of a large excess of alkali. Although these by-products are useful chemicals, they are often less valuable than the halides from which they come and their production interferes with etherification of the cellulose. Their formation, therefore, should be held to a minimum. Hydrolysis of alkyl sulfates under etherifying conditions occurs more readily than that of alkyl chlorides, hence the latter are preferred in commercial operations.

Reaction must be maintained as uniform as possible, a task which

presents difficulties because of the heterogeneity of the system. Where low degrees of etherification are desired, the vapor of alkyl halide is best circulated under pressure through loosely packed alkali cellulose. For higher degrees of etherification, agitation is required. Too vigorous stirring, however, especially at the beginning of reaction, causes excessive formation of by-product alcohols by effecting hydrolysis of the chloride.

Commercial operations are usually carried out in autoclaves at temperatures ranging from 80 to 150°, the time required varying between 5 and 24 hours. After etherification is complete, the product is precipitated, usually by hot water, washed free from salt, and then dried.

The properties of the product are contingent upon four factors, namely:

- (1) the nature of the etherifying radical, (2) the extent of etherification, (3) the degree of polymerization or molecular weight of the product, and (4) the uniformity of etherification.

The nature of the etherifying radical is, of course, readily controlled by selection of the proper halide. The relationships between softening point, moisture absorption, solubility in benzene and character of the alkyl group in ethers of about the same degree of alkylation are indicated by Table 157.

Table 157. Comparative Properties of Cellulose Ethers⁶⁰

Ether	Average Number of Ether Groups per Glucose Unit	Softening Point, ° C	Moisture Absorption, % at 19° and 72% R.H. during 48 Hrs	Solubility in Benzene
Ethyl cellulose	2.15	158	3.001	Insoluble
Butyl cellulose	2.28	65	1.673	Soluble
Amyl cellulose	1.91	45	0.975	Soluble

The extent of etherification depends not only upon the time and temperature of reaction, but also upon the ratio of cellulose to alkali, water to alkali, and alkyl halide to cellulose. In particular, the number of ether groups present in the cellulose derivative depends to a marked extent upon the amount of alkali used. Disubstituted ethers, for example, are produced by holding the alkali concentration constant at 30 to 35 per cent. Most complete and uniform etherification can be obtained by repeated treatments with caustic and halide or by addition of alkali as reaction progresses in order to maintain constant concentration. Because of the gaseous nature of methyl and ethyl chlorides, etherification with these reagents is customarily conducted in autoclaves which cannot be conveniently opened during reaction for occasional addition of alkali. Hence, despite the fact that reaction usually begins more slowly at high alkali concentrations, a considerable excess of caustic, often as solid al-

kali, is used at the beginning so that enough reagent will be present at the end of the reaction to yield the desired extent of etherification.

The softening points and solubilities of cellulose ethers vary markedly, depending upon the number of ether groups present. Figure 292 shows the relation of softening point to this factor in the case of ethyl and benzyl ethers, while Figure 293 indicates the connection between moisture absorption and degree of substitution of ethyl cellulose.

In the case of methyl and ethyl ethers, low degrees of substitution result in alkali solubility; intermediate degrees in water solubility; and high degrees in water insolubility, coupled with solubility in organic solvents of increasingly non-polar character as substitution increases. Butyl and benzyl celluloses are insoluble in water regardless of the number of reacted hydroxyl groups.

Table 158. Relation between Degree of Substitution and Solubility of Ethyl Cellulose ⁶⁰

Substitution Range	Solubility
About 0.5	Alkali (4-8% NaOH)
1.0 (0.8-1.3)	Water
1.4-1.8	Increasing swelling in (organic) polar-non-polar solvent mixtures
1.8-2.2	Increasing solubility in the above type of solvent mixtures
2.2-2.4	Increasing solubility in alcohol and less polar solvents
2.4-2.5	Maximum solubility
2.5-3.0	Rapid drop in alcohol solubility; soluble only in non-polar solvents

The gradual increase in solubility of benzyl cellulose in non-polar solvents as substitution increases is shown in Table 159.

Table 159. Solubility Relations of Benzyl Cellulose ⁶⁰

Substitution per Glucose Unit	Benzene-Alcohol	Benzene	Solubility In Toluene	Xylene
2.0	soluble	partially soluble	swelling	swelling
2.1	soluble	soluble	partially soluble	swelling
2.2	soluble	soluble	soluble	partially soluble
2.3	soluble	soluble	soluble	soluble

It has been pointed out that the reaction between alkali cellulose and alkyl halides occurs in a heterogeneous system. Smoother reaction would take place if a homogeneous solution of cellulose could be established. It has been found practicable to bring about such a condition by using concentrated (35 to 50 per cent) aqueous solutions of organic bases like trimethylbenzyl ammonium hydroxide which dissolve cellulose. Although these reagents are too expensive for general industrial applica-

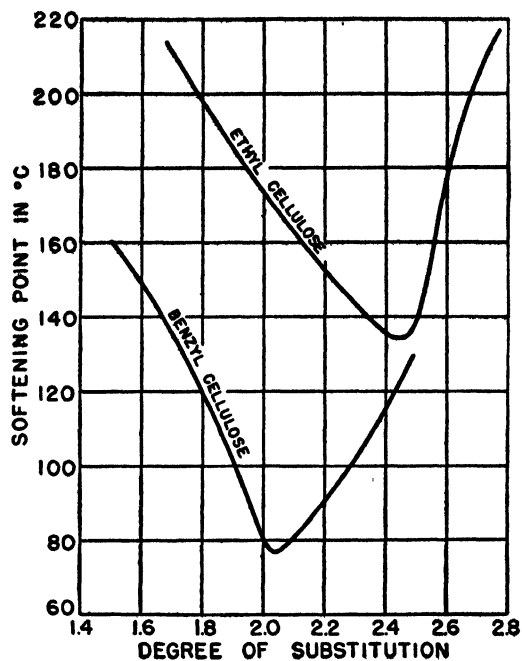


Figure 292. Softening point of cellulose ethers as a function of degree of substitution. (Lorand⁶⁰)

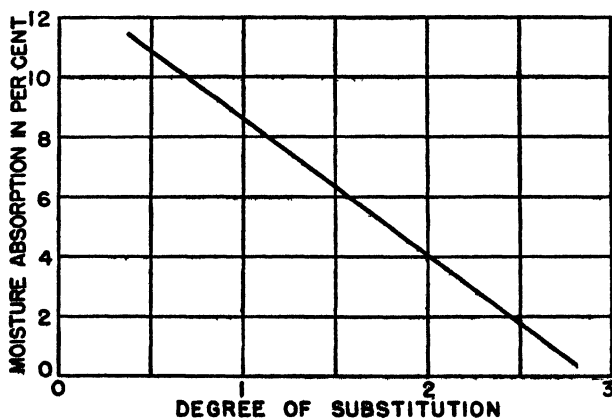


Figure 293. Moisture absorption of ethyl cellulose as a function of degree of substitution. (Lorand⁶⁰)

tion, they do afford a way of obtaining water-soluble ethers of a low degree of etherification. Ethers possessing only 0.6 to 0.7 methyl or ethyl groups per glucose unit are water-soluble if produced by this method, whereas it is necessary to introduce nearly twice this number by the soda cellulose process in order to attain water solubility. Moreover, by use of these organic bases, it is possible to make a water-

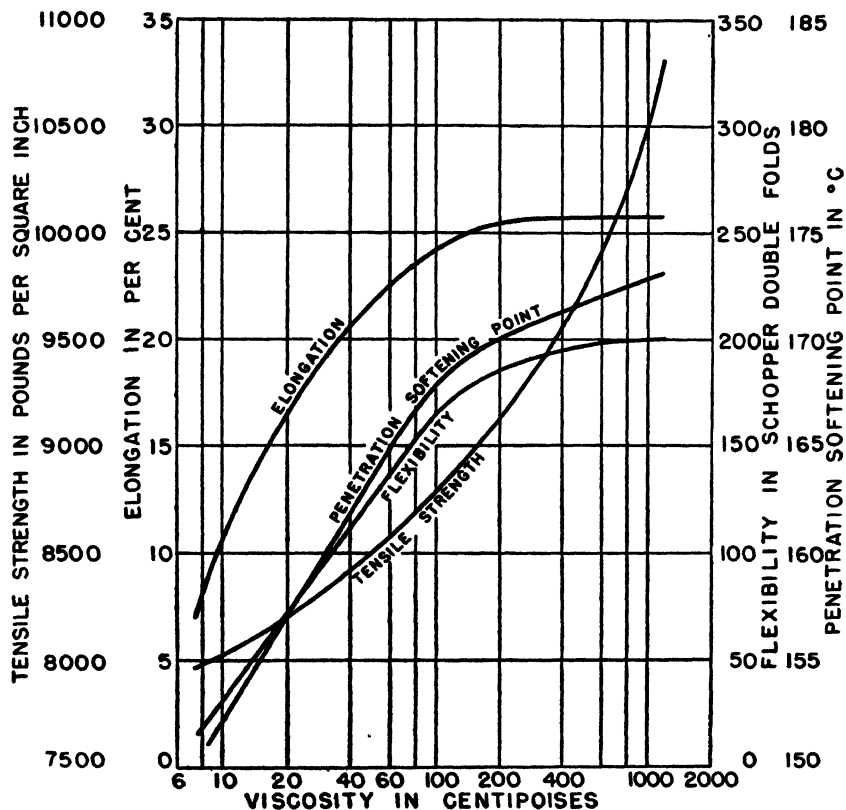


Figure 294. Relation between certain physical properties and the viscosity of 46.8-48.5 per cent ethoxyl (Hercules' N-Type) ethyl cellulose. (Viscosity determined at 5 per cent concentration.) (Hercules Powder Company³⁸)

soluble grade of hydroxyethyl cellulose, a result which cannot be achieved with soda cellulose.

The degree of polymerization of cellulose ethers is directly reflected in the viscosity of their solutions and, consequently, establishes the practical limits for the solids content of lacquers based on these resins. This characteristic is regulated in part by the purification and pretreatment of the cellulose, although extensive molecular break-down takes place under

the conditions of all commercial etherifications. Degradation of cellulose ethers can also be brought about by treating the finished products with mineral acids.

The degree of polymerization of commercial grades of ethyl cellulose is from 200 to 550.

Such mechanical properties as tensile strength, elongation, and flexibility are not greatly affected by the degree of substitution of a cellulose ether, but they are markedly dependent upon its degree of poly-

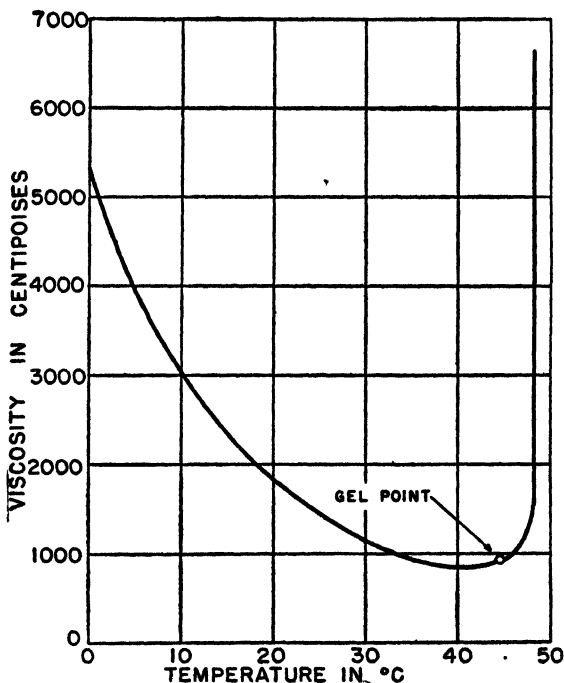


Figure 295. Effect of temperature on viscosity of an aqueous 5 per cent solution of "Methocel," medium viscosity type.

Courtesy The Dow Chemical Company 21

merization, *i.e.*, molecular weight. This fact is shown in Figure 294 in the case of ethyl cellulose.

Methyl Cellulose. Methyl cellulose is produced in several viscosity grades containing from 1.4 to 2.1 methoxyl radicals per glucose unit. The commercial product possesses the unusual distinction among hydrophilic colloids of being soluble in cold water, but insoluble hot. Wetting with alcohol assists aqueous solution. Upon heating, gelation occurs between 40° and 70°, the precise point being a function of molecular weight and concentration. Cooling resolves the gel. Figure 295 illustrates the effect of heat upon methyl cellulose solutions. Inorganic salts, polybasic acids, phenols, and tannins usually precipitate methyl cellulose from solution, but coagulation can often be prevented by addition of al-

cohol, ammonium thiocyanate, or glycol acetate. Solutions of methyl cellulose do not ferment or mildew. Methyl cellulose can be ingested without harm. It is excreted without assimilation and without any substantial alteration in methoxyl content.

Methyl cellulose is used as a thickening agent in the formulation of textile printing pastes. It is recommended as an emulsifying agent, adhesive, and water-soluble film former. Water-resistant films can be prepared by admixture of urea-formaldehyde or melamine-formaldehyde curable resins therewith. Methyl cellulose is also used as a thickening agent in various cosmetic preparations and dentifrices and as an impregnant and size for various types of paper.

Ethyl Cellulose. Ethyl cellulose, the most important of the cellulose ethers, is available in flake form as Dow's "Ethocel" and Hercules' ethyl cellulose. It is produced only in water-insoluble grades of higher degrees of substitution. Materials containing from 43.5 to 50 per cent ethoxyl are available. The most common possess 48.5–49.5 or 46.8–48.5 per cent, depending upon the manufacturer. This degree of etherification corresponds to ethylation of about 2.4–2.5 hydroxyl groups per glucose unit, a point at which optimum solubility in both polar and non-polar solvents is obtained. The theoretical ethoxyl content of the triether is 54.9 per cent. Substitution beyond 50 per cent, however, results in loss of solubility in polar solvents, such as ethanol. It has been noted in a preceding section that certain other properties besides solubility are also dependent upon the degree of substitution.

Ethyl cellulose is available in several average molecular weight grades, or degrees of polymerization, as reflected and rated in terms of viscosity of their solutions in certain specific solvents at certain definite concentrations. Viscosities are usually expressed either as centipoises of 5 or 20 per cent solutions in mixed toluene-ethanol, or as falling-ball seconds of 20 per cent solutions in mixed benzene-methanol. The relation between mechanical properties and degree of polymerization of ethyl cellulose has been discussed in a preceding section.

Since its introduction into this country about 1935, ethyl cellulose has rapidly gained favor in both coating compositions and molded plastics because of several advantages which it possesses over other cellulose plastics. It is resistant to both weak and strong alkalis as well as dilute acids. It is unusually tough and flexible and, suitably plasticized, retains these characteristics even at temperatures as low as -40° . For any given flow qualities and rigidity, it requires less plasticizer than either cellulose acetate or nitrate, 20 per cent imparting properties to molding compositions similar to those obtained with 30 to 35 per cent of plasticizer with acetate or nitrate. Its range of compatibilities is considerably greater than that of either cellulose acetate or nitrate, almost

any of the usual ester type plasticizers and many oils affording satisfactory properties and being retained well.

Numerous solvents can be used to dissolve it, as shown by Table 160. The influence of degree of substitution upon solubility in several liquids is illustrated in Figure 296.

Table 160. Solubility of 46.8–48.5% Ethoxyl Content Ethyl Cellulose in Representative Organic Solvents ²³

Solvents	5 g Ethyl Cellulose 95 cc Solvent		16 g Ethyl Cellulose 84 cc Solvent	
	Solubility	Clarity	Solubility	Clarity
<i>Alcohols</i>				
Methyl alcohol	S	Haze	S	Haze
Ethyl alcohol	S	Sl. haze	S	Haze
Propyl alcohol	S	Sl. haze	S	Haze
Isopropyl alcohol	S	Sl. haze	SW	—
Butyl alcohol	S	Sl. haze	S	Haze
Amyl alcohol	S	Sl. haze	S	Haze
Cyclohexanol	PS	—	PS	—
Benzyl alcohol	S	Clear	S	Clear
Diacetone alcohol	PS	—	SW	—
<i>Esters</i>				
Methyl acetate	S	Sl. haze	S	Haze
Ethyl acetate	S	Sl. haze	S	Sl. haze
Propyl acetate	S	Sl. haze	S	Sl. haze
Isopropyl acetate	S	Haze	S	Haze
Butyl acetate	S	Sl. haze	S	Sl. haze
Amyl acetate	S	Sl. haze	S	Sl. haze
Methyl "Cellosolve" acetate	S	Sl. haze	S	Sl. haze
"Cellosolve" acetate	S	Sl. haze	S	Haze
Glycol diacetate	S	Clear	PS	—
Benzyl acetate	S	Sl. haze	S	Sl. haze
Cyclohexyl acetate	S	Haze	PS	—
Methyl formate	S	Sl. haze	S	Sl. haze
Ethyl formate	S	Sl. haze	S	Sl. haze
Ethyl lactate	S	Sl. haze	S	Sl. haze
Butyl lactate	S	Clear	S	Sl. haze
<i>Ethers</i>				
Ethyl ether	SW	—	S	Haze
Methyl "Cellosolve"	PS	—	PS	—
"Cellosolve"	S	Haze	S	Haze
Butyl "Cellosolve"	S	Haze	S	Haze
"Carbitol"	SW	—	SW	—
<i>Ketones</i>				
Acetone	S	Haze	S	Haze
Methyl ethyl ketone	S	Sl. haze	S	Haze
Dipropyl ketone	S	Haze	PS	—
Hexone	S	Haze	S	Haze
Cyclohexanone	S	Sl. haze	S	Sl. haze
Methyl cyclohexanone	S	Clear	S	Sl. haze
<i>Miscellaneous Solvents</i>				
Dichloroethyl ether	S	Haze	PS	—
Anisole	S	Sl. haze	S	Sl. haze
Dioxane	S	Sl. haze	S	Sl. haze
Pine oil	S	Clear	S	Clear
"Hercosol" 80	S	Clear	S	Clear

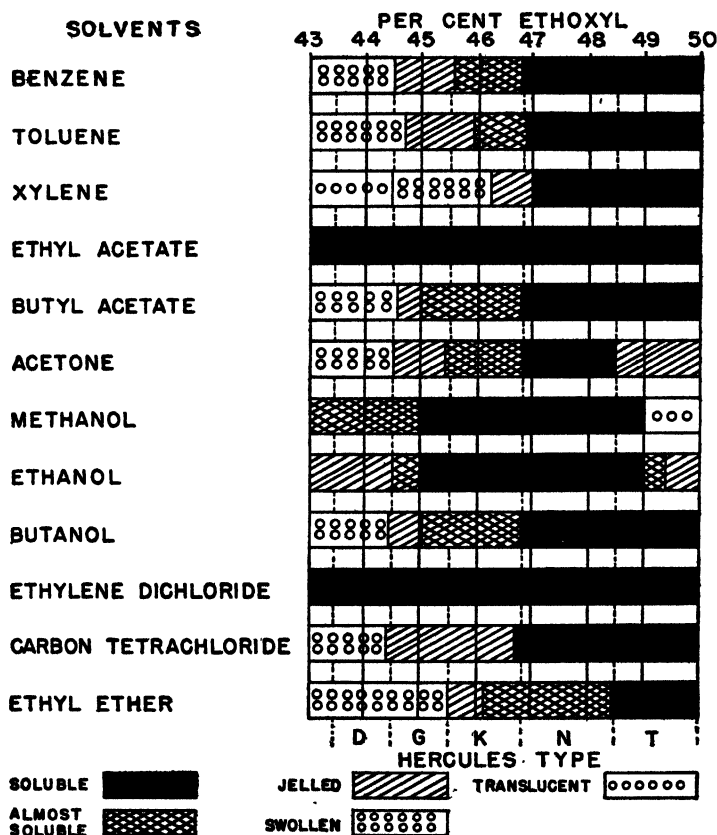
Hydrocarbons				
Benzene	S	Clear	S	Clear
Toluene	S	Clear	S	Clear
Xylene	S	Clear	S	Clear
Hi-flash naphtha	PS	—	PS	—
Cyclohexane	S	Clear	S	Clear
Tetralin	S	Clear	S	Clear
Dipentene	SW	—	PS	—
Turpentine	SW	—	SW	—
Hydrogenated naphthas and petroleum distillates containing cyclic hydrocarbons ("Solvessos," "Union" solvents, "Shell" solvents, "Solvols," etc.)	PS	—	PS	—
Petroleum ether	I	—	I	—
Hexane	I	—	I	—
V. M. & P. naphtha	I	—	I	—
"Varsol"	I	—	I	—
Chlorinated Hydrocarbons				
Methylene chloride	S	Clear	S	Clear
Chloroform	S	Clear	S	Clear
Carbon tetrachloride	S	Clear	S	Clear
Ethylene dichloride	S	Sl. haze	S	Sl. haze
Trichloroethylene	S	Sl. haze	PS	—
Pentachloroethane	S	Clear	S	Clear
Mixed Solvents				
Benzene 80-methanol 20	S*	Clear	S*	Clear
Toluene 80-ethyl alcohol 20	S*	Clear	S*	Clear
Xylene 80-butanol 20	S*	Clear	S*	Clear
Ether 66 $\frac{2}{3}$ -ethyl alcohol 33 $\frac{1}{3}$	S	Haze	S	Haze
Ethyl alcohol 15-camphor 1	S	Haze	S	Haze
Turpentine 70-butanol 30	S	Clear	S	Clear
Dipentene 70-butanol 30	S	Clear	S	Clear
Hydrogenated naphthas and petroleum distillates containing cyclic hydrocarbons "Solvessos," "Union" solvents, "Shell" solvents, "Solvols," etc.) 70-butanol 30	S*	Clear	S*	Clear
S-Soluble	PS-Partly Soluble	SW-Swollen	I-Insoluble	

* These solvent mixtures are the most generally useful because they combine good clarity with low viscosity and are economical. Although many solvents produce slightly hazy or hazy solutions, the films obtained from these are clear in a majority of cases.

Ethyl cellulose is compatible with certain natural resins such as de-waxed dammar, elemi, kauri, and rosin, and with oil soluble phenolics, ester gum, and alkyds modified with phenol and rosin. Its compatibility with other types of alkyds is limited. It is compatible with nitrocellulose in all proportions, a fact which permits its use with nitrocellulose lacquers as a pigment grinding base. It is, however, incompatible with cellulose acetate and acetate butyrate. It is not compatible with acrylates, vinyls, polystyrene, or polyisobutylene.

Ethyl cellulose possesses low flammability. It also shows good reten-

tion of transparency upon aging, although crystal and light tints are not readily attained in molding powders. Some oxidative degradation, however, occurs upon continued exposure to ultraviolet light or to temperatures in excess of 150°. Although color is not affected thereby, em-



Courtesy Hercules Powder Co.⁸⁸

Figure 296. Effect of substitution on the solubility of ethyl cellulose in various organic solvents. The broadest solubility occurs in the region of about 46.8 to 48.5 per cent ethoxyl. (Tests made on 15 per cent solutions.)

brittlement takes place so that ethyl cellulose formulations which are to be exposed to these conditions should be stabilized by addition of about one per cent of an antioxidant.

The density of ethyl cellulose is 1.14, lower than that of any other cellulose derivative and among the lightest plastics.

Physical properties of unplasticized ethyl cellulose are listed in Table 161.

Ethyl cellulose molding powders can be prepared by compounding on hot rolls or in heated Banbury mixers without the use of solvent—plasticizers and coloring materials being added directly.

Table 161. Physical Properties of Ethyl Cellulose²⁸

Specific gravity	1.14
Refractive index	1.47
Color	Colorless
Taste	None
Odor	None
Tensile strength, lb/sq in (dry)	6000–15,000
Tensile strength, lb/sq in (wet)	80–85% of dry strength
Elongation	10–40%
Melting point	190–200° C.
Softening point	140–150° C.
Light transmission	Transparent down to 2800Å (passes sunlight)
Moisture vapor permeability, g/sq cm/cm/hr	6.4×10^{-4}
Moisture absorption (80% relative humidity for 24 hours)	2.0%
Modulus of elasticity, lbs/sq in	1.89×10^5
Flexibility, Schopper double folds	60–100 folds
Hardness Index, Sward, % of glass	71%
Specific surface resistivity (ohms $\times 10^{-10}$), 70 hours at 30° and 78.7 relative humidity	2000
Dielectric strength (A.S.T.M. method) (10 mil film) volts/mil	1500
Dielectric constant 25°–1000 cycles	3.9
Dielectric constant 25°–60 cycles	2.6
Power factor 25°–1000 cycles	0.0025
Power factor 25°–60 cycles	0.0030

Because of their thermoplastic character, ethyl cellulose molding powders are used principally for injection molding and extrusion, including wire coating. Typical properties of injection and extrusion grades of "Ethocel" plastic are given in Tables 162 and 163.

Molding powders are available under the trade names "Ethocel" and "Lumarith" EC. Prices averaged 52–54 cents per pound for plain colors in 1944.

Ethyl cellulose plastics can be easily machined, swaged, and cemented.

Sheets, film, and foil of ethyl cellulose, known especially under the name, "Ethofoil," have entered the packaging field to a limited extent, as well as electrical insulation. Electrical properties of 10-mil ethyl cellulose films are listed in Table 164 and compared with cellulose acetate of similar thickness.

The yield point and hence the hardness of unplasticized ethyl cellulose film is only slightly affected by the degree of polymerization of the resin, but elongation, flexibility, and toughness increase with viscosity. The effect of the amount of plasticizer upon the stress-strain curves of

Table 162. Properties of Injection Grades of "Ethocel" Plastic ²⁰

Property*	IR-H	IR-MS	IR-S ₂
Molding:			
A.S.T.M. Flow Rating	H	MS	S ₂
Injection Molding Temperature	350° F	330° F	315° F
Injection Molding Pressure, lb/sq in	3500	3500	3000
Apparent Volume of Granules, cu in/lb Approx.	40	40	40
Specific Gravity, 70° F	1.15	1.15	1.16
Mold Shrinkage, inches/inch	.002	.002	.002
Thermal:			
Specific Heat, cal/g/° C			
At 21° (70° F)	0.3	0.3	0.3
At 149° (300° F)	0.55	0.55	0.55
Distortion Temperature, ° F	187	165	158
Heat Shrinkage, inches/inch, 70° to 170° F			
24 Hours	.004	.004	.007
7 Days	.005	.005	.009
Cold Shrinkage, inches/inch + 70 to - 40° F	.001	.001	.002
Mechanical:			
Tensile Strength, lb/sq in	9000	7500	6000
Elongation, %	4.7	6.0	9.5
Impact Strength (Izod), ft lbs/in notch	8.2	7.4	8.0
Rockwell Hardness (superficial), ½ in ball, 15 kg load	85	80	74
Water Absorption, (24 hrs immersion at 70° F), % by weight	1.5	1.4	1.3
Material Extractable by Water in Above Test	None	None	None
Electrical:			
Dielectric Strength, volts/mil at .010 inch	1400	1500	1700
Power Factor			
1,000 cycles, %	2.24	2.85	3.80
1,000,000 cycles, %	2.10	2.70	2.90
Dielectric Constant,			
1,000 cycles	3.67	3.78	3.98
1,000,000 cycles	3.37	3.20	3.50

* Dow's "Lt Ethocel" possesses improved low-temperature characteristics.

Table 163. Properties of Extrusion Grades of "Ethocel" Plastic ²⁰

Property	ER-S	ER-S ₂	ER-S ₃
Molding:			
A.S.T.M. Flow Rating	S	S ₂	S ₃
Extrusion Temperature, ° F	360	350	340
Specific Gravity, 70° F	1.16	1.16	1.17
Physical Properties:			
Tensile Strength, lb/sq in	4500	4200	4000
Yield Point, lb/sq in	3500	3000	2200
Elongation, %	45	55	65
Rockwell Hardness (Superficial), ½" ball, 15 kg load	86	75	68
Wet Strength, lb/sq in	4000	3500	3000
Water Absorption (24 hrs immersion) at 70° F, % by weight	1.5	1.4	1.2
Burning rate (A.S.T.M.), in/min	1.2	0.9	0.9
Dielectric Strength, Volts/mil at .010 in	—	—	—

Table 164. Electrical Properties of Ethyl Cellulose ⁵³

Property	10-Mil Film	
	Ethyl cellulose	Cellulose acetate
Dielectric strength (A.S.T.M. method), volts/mil	1500	1400
Dielectric constant:		
1000 cycles	3.9	5.7-7.0
60 cycles, 25°	2.6	—
60 cycles, 100°	2.9	—
Power factor, %:		
1000 cycles	0.25	0.50
60 cycles, 25°	0.3	—
Specific surface resistivity (conditioned 70 hr at 78% relative humidity and 30°), ohms $\times 10^{-10}$	2000	15

ethyl cellulose films plasticized with certain phthalates is shown in Figures 297 and 298.

Non-solvent type plasticizers, such as *n*-butyl stearate, result in an exceptionally large decrease in yield point together with somewhat decreased elongation. Flexibility of ethyl cellulose is not greatly improved until considerable amounts—usually 40 per cent or more—of plasticizer is added if the latter is of the non-solvent type. Such plasticizers also sweat out to the surface on heating.

Table 165 gives the properties of ethyl cellulose films, plasticized with various materials, after two weeks of heating at 70°.

Table 165. Properties of Plasticized Ethyl Cellulose Films After Heating 2 Weeks at 70° ⁵

Plasticizer	Yield Point kg/sq cm	15% Foil Heated 2 Weeks at 70°		Approx. Plasticizer Loss %
		Elongation %	Tensile Strength kg/sq cm	
Blank	470	31	635	0
Triphenyl phosphate	330	25	390	0
Tricresyl phosphate	360	35	500	0
Diphenyl mono- <i>o</i> -xenyl phosphate	365	35	495	0
Monophenyl di- <i>o</i> -xenyl phosphate	450	35	580	0
Tri- <i>o</i> -xenyl phosphate	460	35	575	0
Diethyl phthalate	420	30	520	60
Dibutyl phthalate	380	45	590	20
Diphenyl phthalate	400	35	570	0
Dimethoxyethyl phthalate	390	35	540	50
Methyl phthalyl ethyl glycolate	430	20	480	80
Ethyl phthalyl ethyl glycolate	400	30	480	60
Butyl phthalyl butyl glycolate	355	25	400	0
<i>o,p</i> -Toluenesulfonanilide	440	30	550	10
Ethyl- <i>o,p</i> -toluenesulfonamide	470	25	525	90
Methyl abietate	550	4	550	—
Hydrogenated methyl abietate	510	4	510	—
Castor oil (AA cold-pressed)	325	38	480	0
<i>n</i> -Butyl stearate	345	25	405	30

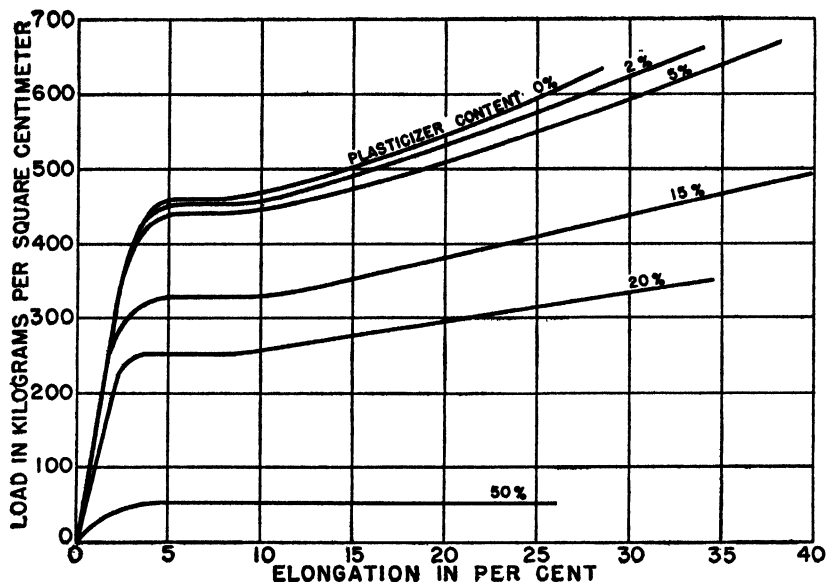


Figure 297. Effect of amount of dibutyl phthalate on physical properties of ethyl cellulose film. (Plasticizer content in per cent by weight of 75 cps "Ethocel.") (Bass and Kauppi⁶)

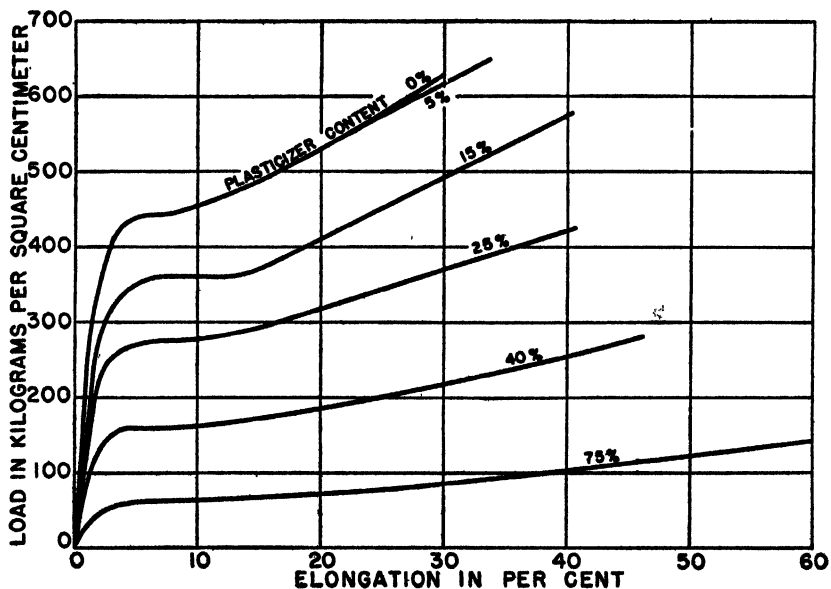


Figure 298. Effect of amount of diphenyl phthalate on physical properties of ethyl cellulose film. (Plasticizer content in per cent by weight of 75 cps "Ethocel.") (Bass and Kauppi⁶)

The various principles just discussed are of importance also in the formulation of surface coatings—one of the earliest applications of ethyl cellulose and still an important use. Such coatings are somewhat more sensitive to water than those of nitrocellulose, but this situation can be corrected by incorporation of other water resistant resins or waxes in the coating. They possess good color stability in sunlight. They are resistant to cold checking, one of the reasons for which ethyl cellulose is sometimes added to varnishes based on other vehicles.

Special uses of ethyl cellulose coatings include resin-treated fabrics and resin-coated yarns such as "Plexon," artificial leather, and resin-finished paper.

Ethyl cellulose is used as a grinding base for dispersing pigments in lacquers, enamels, and printing inks; not only in those utilizing this resin, but others as well, especially those containing cellulose nitrate. Excellent pigment dispersion in solid resin can be obtained on heated rubber rolls. The color chips are broken up and added to the lacquer.

A product which was developed soon after Pearl Harbor is a highly plasticized, flexible, and more or less elastic material known as "Ethyl Rubber." Any one of many plasticizers, mostly oils, may be used to the extent of 40 to 60 per cent of the total composition. Castor oil appears to be preferred. These materials are unsuitable for use at higher temperatures because of their thermoplastic nature. Their use with solvents must be carefully watched, also, to avoid contact with liquids capable of dissolving either resin or plasticizer. Characteristics of a few "Ethyl Rubber" compositions proposed by Hercules Powder Company are listed in Table 166.

Ethyl cellulose has been extruded on an experimental scale as "Ethorayon," but this variety of artificial silk has not been developed commercially.

The unusual compatibility of ethyl cellulose with other resins and waxes has resulted in development of a hard, tough, heat fusible and reusable casting composition known under the name "Thermocast." It has found use in forms employed in shaping aluminum aircraft parts. A similar product for use in the tooling field is available under the designation "Ethocel" TF (for thermoforming). This material is sold in a variety of colors with pour temperatures ranging from 340 to 395° F.

Ethyl cellulose is also available under the trade-mark "Stripcoat" for application as a hot melt type of protective coating for the preservation of metal parts. The optimum temperature for the dipping tank in the use of this material is 375° F. Ethyl cellulose has been proposed as a binder for thermoplastic cloth laminates in such applications as air vents and fairings.

CELLULOSE PLASTICS

703

Flexibility at - 20°:
Number Double Folds (M.I.T. Flex Tester)

Flexibility at Approximately - 78°:
(Pinch Test)

Burning Rate:
Seconds for 3-inch Length

Effect of Gasoline on Plastic:
(after 24 hrs)

(after 48 hrs)

Effect of S.A.E. 90 Motor Oil:
(after 24 hrs)

(after 48 hrs)

Effect of 1% Na₂CO₃ Solution:
(after 24 hrs)

(after 48 hrs)

Effect of Butter:
(after 24 hrs)

(after 48 hrs)

Effect of Cheese:
(after 48 hrs)

(after 90 hrs)

Legend: B = brittle
Bl = blushed
C = clear
Che = cheesy

F = flexible
H = hazy
NB = non-burning
SC = surface cracking

Sf = soft
SSf = slightly soft
SSW = slightly swollen
St = sticky

Sw = Swollen
U = unaffected
VH = very hazy
W = wrinkled excessively

1280	170	3	500	160	19	65,000 +	Sample too thick
B	B	B	F	F	F	F	B
NB	71	NB	NB	NB	46	20	66
Sf	Sf	Sf	Sf	Sf	SSf	EW	BW
Sw	Sw	Sw	Sw	Sw	Sw	BSw	BSw
St	St	St	St	St	SSf	BW	BW
Sf	Sf	Sf	Sf	Sf	Che	BSw	BSw
Sw	Sw	Sw	Sw	Sw	SSw	SSw	Sw
St	St	St	St	St	U	W	F
U	U	U	U	U	U	W	F
U	U	U	U	U	U	U	U
Bl	Bl	U	Bl	Bl	U	U	U
Bl	Bl	U	Bl	Bl	U	Sw	Sw
U	U	U	U	U	U	BSw	Sw
U	U	U	U	U	U	5 min	7 min
F	F	F	F	F	F	Failed	Failed
F	F	SC	SC	SC	F	Failed	Failed

Other Ethers of Cellulose. Benzyl cellulose has been made on an experimental scale in the United States, but it has not acquired industrial status, largely because the economics of production are not favorable.

Hydroxyethyl cellulose, available under such trade-marks as "Cello-size" and "Sylsize," can be obtained either by metathesis between ethylene chlorohydrin and alkali cellulose or by direct reaction of ethylene oxide upon cellulose itself. An alkali-soluble grade is produced under the trade name, "Ceglin," and is marketed for use as a permanent finish for textiles.

Carboxymethyl cellulose is available in the form of its sodium salt. It is sold for many purposes, especially for textile applications under such trade names as "Carboxymethocel," "Collocel," and "CMC." This product is also used to impart a fine texture to ice cream.

Finally, it has been found possible to etherify partially the cellulose of woven cotton fabrics, thus rendering the goods water-repellent. First produced in England under the name "Velan" and now marketed here as "Zelan," stearoxy-methyl-pyridinium chloride has found use for this purpose. When "Zelan"-treated cotton is warmed, reaction occurs readily and stearoxymethyl groups may be introduced into surface layers of the cellulose molecules.

Regenerated Cellulose

"There might be a way found out to make an artificial glutinous composition much resembling, if not fully as good, nay better, than that excrement or whatever other substance it be out of which the silk-worm wire-draws his clew."—Hooke's *"Micrographia,"* 1665

This theme was resurrected in 1734, by the French naturalist, de Réaumur, but another 150 years passed before Swann in England and de Chardonnet in France produced the first synthetic fibers in which nitrocellulose served as the "artificial glutinous composition" resembling natural silk. During the latter part of the nineteenth century and the first two decades of the present one, several cellulose derivatives were spun into artificial silk. Progress was at first slow because of many technical difficulties, as well as because the filaments possessed poor wet strength and certain other adverse characteristics. In 1910 the Viscose Company began operation of the first American plant for the production of artificial silk, turning out 181 tons during the first year. A committee of silk manufacturers appointed about that time to investigate the potential threat of this new material to its well established markets reported that artificial silk was so harsh in feel and so readily weakened

by water that there existed no possibility for it ever to find extensive use in the textile industry!

Constant technologic advances, however, resulted in improvement of quality, attended by increased consumer demand. In 1924, a progressive department store official drew attention to the poor psychological impression produced by the term *artificial silk* and urged the adoption of a more euphonious name which would connote a new material instead of a cheap substitute. A committee representing producers of the yarn, knitters, weavers, and the National Retail Dry Goods Association was quick to seize upon this suggestion and adopted the designation *rayon*, a word which had a pronounced effect upon public demand.

With the passage of the years, other kinds of fibers, both semi-synthetic and synthetic, were introduced so that the Federal Trade Commission was called upon to define rayon as follows: "The word Rayon is the generic term for manufactured textile fiber or yarn produced chemically from cellulose or with a cellulose base and for thread, strands, or fabrics made therefrom, regardless of whether such fiber or yarn be made under the viscose, acetate, cuprammonium, nitrocellulose, or other process."

The first successful form of synthetic fiber was developed in France in 1884 by Count Hilaire de Chardonnet. It consisted of strands of nitrocellulose produced by squirting a collodion-like solution through a spinneret and evaporating the solvent as it emerged on the outlet side. It was soon found that the high flammability of this material made its use extremely hazardous. Search for a method of eliminating this danger resulted in a process of denitration, brought about by passing the spun nitrocellulose into a dilute aqueous solution of alkali hydrosulfides at about 40°. Hydrolysis occurred readily and the product, often referred to as *Chardonnet* or *nitro silk*, was in fact a regenerated form of cellulose. It enjoyed popularity for many years, but other kinds of artificial silk gradually pushed it into the background. Manufacture in this country ceased in 1934.

Another process for making artificial silk, likewise secondary today, is based upon the use of Schweitzer's reagent, an ammoniacal solution of copper oxide, which readily dissolves cellulose. The solution is spun by passage through the usual spinneret into an acid bath which reprecipitates the original cellulose. This type of rayon was developed by a Frenchman, Despeissis, but is best known under the German names of "Glanzstoff" and "Bemberg silk." "Bemberg" has also been produced in the United States for many years and is still currently available.

By far the most important variety of artificial silk at the present

time is viscose, a product which was developed by the British chemists C. F. Cross, E. J. Bevan, and C. Beadle, who obtained the earliest patents in this field in 1892. Current production of viscose corresponds to about



Courtesy American Viscose Corp.

Figure 299. Placing pulp sheets in caustic soda steeping presses in the manufacture of viscose.



Courtesy American Viscose Corp.

Figure 300. Charging crumbing machine with steeped pulp.

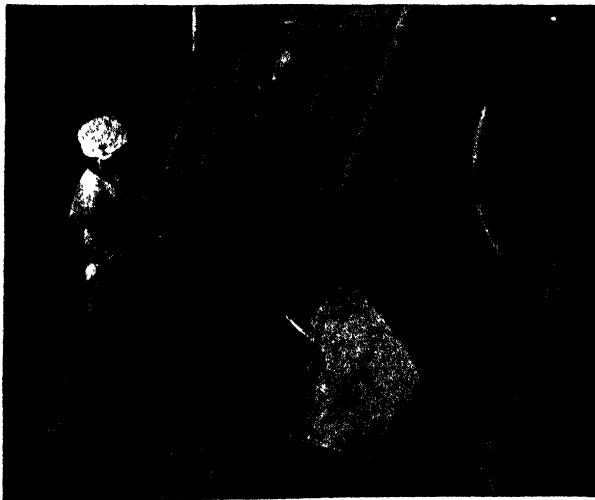
two-thirds of the total amount of rayon manufactured in the United States.

The exact nature of the chemical reactions which occur during the manufacture of viscose is still uncertain. Operations begin with the



Figure 301. Crumbing machine discharging alkali cellulose crumbs.

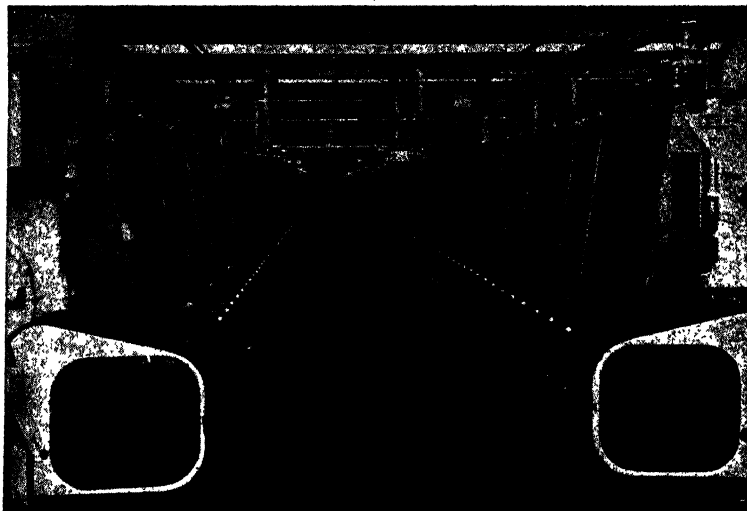
Courtesy American Viscose Corp.



Courtesy American Viscose Corp.

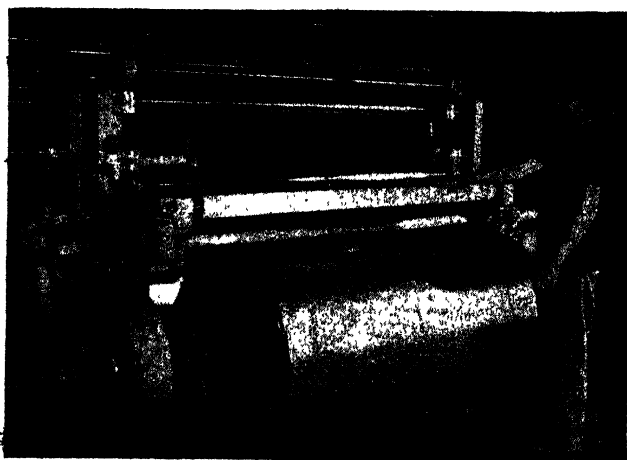
Figure 302. Churn discharging cellulose xanthate crumbs.

formation of alkali cellulose as in the manufacture of cellulose ethers. Purified and bleached alpha-cellulose from wood pulp, usually sulfite pulp from spruce, fir, or western hemlock, is ordinarily employed, but



Courtesy American Viscose Corp.

Figure 303. Viscose spinning machines.

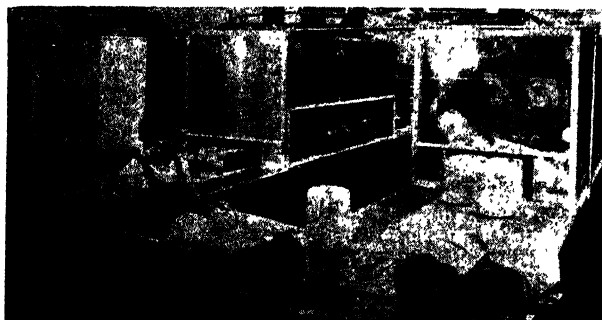


Courtesy American Viscose Corp.

Figure 304. Beaming viscose yarn. Tirecord warp.

cotton may also be used either alone or admixed with wood cellulose. After steeping in 17 to 18 per cent caustic for a period ranging from 30 minutes to 2 hours and at 15–20°, excess alkali solution is expressed until

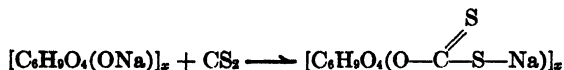
the original cellulose is wet with only about twice its weight of liquor. During the steeping operation, approximately sixteen times as much caustic solution, by weight, as cellulose is employed. The wet, pressed, alkali cellulose is then shredded into fine crumbs which are allowed to age at 20–25° for two or three days. During this time, considerable molecular degradation occurs. The necessary quantity of carbon disulfide is then added to the alkali cellulose in a rotary churn or tumbling barrel, often called a baratte (French for churn), and these reactants are thoroughly mixed together at room temperature for 2 to 4 hours. Dur-



Courtesy The Girdler Corp.

Figure 305. Two tunnels powered by "Thermex" high frequency unit. Rayon tire cord is twist-set this way in a process developed by Industrial Rayon Corporation.

ing this process the temperature must not exceed 30° and reaction must not proceed so far that the crumbs tend to cake. The final product is brownish-red in color. It is cellulose monoxanthate. Its formation can be most simply expressed as follows:



Probably both alkali cellulose and cellulose xanthate are actually more complex than represented here. A trixanthate can be produced experimentally by using solutions of cellulose in organic ammonium hydroxides.

The xanthate is now dissolved in sodium hydroxide solution, the resulting liquor being known specifically as viscose. It is allowed to stand at 15–20° for some time, usually from two to five days. This process is known as ripening. Here again the chemical reactions which occur are not clearly understood, but sulfur splits out from the viscose in the form of soluble inorganic sulfides and thiocarbonates, resulting in a decrease of the number of xanthate groups from an average of about

one for every glucose unit to about one for every four glucose units. As ripening proceeds, viscosity first decreases, then increases, and finally gelation occurs. Figure 306 shows this effect.

After control tests indicate that ripening has progressed far enough, the viscose solution is filtered, subjected to vacuum to eliminate any bubbles which might be entrapped in the spinneret and interrupt filament

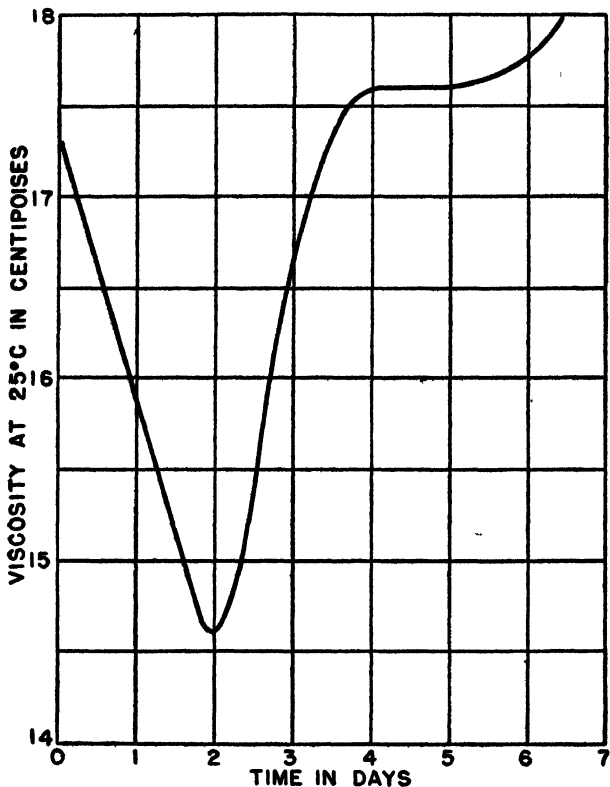


Figure 306. Change in viscosity of wood pulp viscose during ripening at 25°. (*Compton*¹⁸)

formation, and then spun into a precipitating bath of acidic nature usually containing sulfuric acid and sodium sulfate, with or without other sulfates such as those of ammonia or zinc, and other additives such as glucose. Incidentally, some 40 million pounds of glucose are consumed every year in the manufacture of viscose silk.

The spinnerets are usually constructed of platinum. The orifices in the spinneret vary from 0.002 to 0.003 inch, depending upon the denier desired. All of the monofilaments issuing from a single spinneret are

mechanically combined into a single thread of viscose rayon yarn. Numerous operations are then carried out, including desulfurizing, rinsing, bleaching, washing, stretching, and drying.

Control of the time and temperature of reaction and of the concentration of solutions, including the concentration of salts formed during the process as a result of the various reactions, must be carefully maintained throughout the manufacture of viscose silk.

Dull filaments can be produced by adding delustering agents such as titanium dioxide or certain oils to the viscose before spinning.

High-strength viscose is manufactured by using cotton as the initial raw material and by orienting the molecular crystallites of the product by cold stretching. High-strength viscose rayon, such as "Cordura," is utilized for example in the manufacture of tire cord for heavy duty civilian and military motor vehicles, and in the production of fabrics for parachutes used in dropping flares and fragmentation bombs and in mine laying.

In 1941, the total American production of rayon yarn was slightly more than 450 million pounds, of which about 285 million was viscose. Approximately 70 per cent of the viscose was delustered. It is of interest to note that only the manufacture of soap exceeds the viscose industry in the amount of alkali consumed annually.

High-strength rayon produced by regenerating cellulose from acetate has been mentioned earlier in this chapter.

Viscose has been used in the production of several other types of materials which are now almost indispensable to modern living. Among these products, transparent regenerated cellulose sheeting, commonly known as cellophane, ranks first. The machine now used for casting cellophane film was invented by the Frenchman, J. E. Brandenberger, in 1911. A viscose solution is extruded through an elongated orifice onto a moving belt which quickly carries it into a precipitating bath of ammonium or sodium sulfate and dilute sulfuric acid. The regenerated cellulose film is subsequently passed through various washing, desulfurizing and bleaching baths. While still wet, it is conducted through a solution of glycerol. The latter is picked up by the cellophane and acts as a plasticizer. The film is finally dried by passage over heated rolls. It can be moisture-proofed by coating with a very thin film—about 0.00006 inch thick—of low viscosity nitrocellulose plasticized and compounded with natural resins and waxes and dissolved in an organic solvent.

Moistureproof cellophane passes about 270 mg of water vapor per sq in per hr at 100° F. Strength characteristics at 60 per cent relative humidity and 70° F are given in Table 167.

Table 167. Relative Strengths of du Pont Cellophane and Other Papers ⁴⁷

Material	Thickness (inches)	Weight Required to Break 1½-Inch Strip (Scott Machine)		Bursting Strength (Mullen Tester) (lbs/sq in)
		Longitudinal direction (lbs)	Transverse direction (lbs)	
Cellophane	0.00098	15.7	7.3	26.9
Cellophane	0.00141	19.7	8.8	33.8
Cellophane	0.00193	26.8	13.2	42.1
Sulfite paper	0.00162	13.7	7.7	6.1
All-rag high-grade paper	0.00212	22.5	14.5	21.6
Sulfite bond paper	0.00296	43.0	23.2	24.9
Extra high-grade paper	0.00412	73.1	55.5	84.4

Water vapor and water-soluble gases readily diffuse through cellophane. Sparingly soluble gases penetrate much less readily. Ammonia, for example, diffuses through it some 4000 times as rapidly as hydrogen.

Regenerated cellulose film was first produced in France in 1908. In 1924 American manufacture began and its cost thenceforth decreased rapidly to its present level of about 33 cents per pound (41 cents for moistureproof material) which is about one-eighth of its 1924 price. It has been estimated that 1937 saw the production of 80,000,000 pounds of cellophane, a figure which has been greatly exceeded since then. About four-fifths of this amount was moistureproofed.

Regenerated cellophane film is available in several thicknesses under the names "Du Pont Cellophane," "Sylvania Cellophane," and "Sylphrap." Common gauges are 300, 450, and 600, corresponding to thicknesses of 0.00088, 0.0012, and 0.0017 inches, respectively. It is not only available in colorless grades, but also in colors applied by dyeing with either direct colors or mordant dyes. It is embossed in "linen," "silk," "morocco," and other finishes. Wrapping and packaging applications of cellophane, legion in number, are well known and, during World War II, became as important in military as in civilian employ.

Coated with an adhesive mass comprising rubber and various compatible resins such as rosin or hydrogenated rosin and coumarone or hydrogenated coumarone resins, cellophane is used in the manufacture of transparent pressure-sensitive cellulose tape like "Scotch Tape" and "Texcel."

Thin, transparent seamless tubing of regenerated cellulose is manufactured under the name "Visking" for use as sausage casing which, although edible, is not assimilated by the body and is usually removed before eating. Since it does not stick, it is used in making skinless wieners.

Cellulose sponge is made by stirring lumps of sodium sulfate into

solutions of viscose, coagulating, and washing out the sulfate. It also consists of regenerated cellulose.

A recent development is "Bubblfil," a continuous string of gas-filled bubbles or cells of regenerated cellulose, each cell being joined to the one next to it, at either end, through a restricted solid area which forms the neck of each bubble. This material has been produced on a pilot plant scale and has found some use as a substitute for kapok in Army mattresses. It may acquire importance in civilian fields of upholstery and insulation, although it is subject to the objection that upon aging, especially under pressure, deflation of the bubbles occurs. Embrittlement upon soaking in water and subsequent drying, probably the result of plasticizer loss, is a further defect which has prevented its use in life jackets.

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Chapter 23

Lignin Plastics

Much has been written in recent years concerning the utilization of wastes from farm and forest in the manufacture of plastics. In this chapter attention will be directed only to those products which are based upon the lignin content of woody matter. The prodigious annual tonnage of bagasse, cornstalks, cereal hulls, and wastes from lumbering and paper making operations is staggering indeed. In the discussion of plastics derived from these sources, however, fancy must be tempered with reason. The total volume of these wastes surpasses the entire production of the plastics industry by many fold. The properties obtainable in such plastics are limited by the inherent characteristics of the natural substances from which they are made and very definite limitations are thereby placed upon their general applicability. Furthermore, because of these limitations, their utility must in large part be predicated upon low cost, a factor which has to be directly reflected in cheap processing operations. Although the past quarter of a century has seen much research in the field of utilization of agricultural wastes, only a few plastics derived from these sources have as yet become commercial realities and their tonnage is small. Among them all, the most conspicuously successful products are those obtained from sulfite paper mill effluents. Here another incentive has been added to economic utilization of a waste, namely, elimination of objectionable or illegal stream pollution. Other lignin plastics have been made from digested and exploded wood chips, from soda and sulfate paper mill wastes, from redwood sawdust, and from bagasse, although the present commercial status of all these other products is not clear. Acid lignin is obtained in Europe as a by-product of wood sugar operations. A domestic West Coast project may result in American production of this by-product, but it is not used in current plastics applications. Each of these commercial materials will be discussed separately, but a few words should be said about lignin itself.

Lignin

Chemical Nature of Lignin. The composition of wood varies according to source. Partial analyses of four types are given in Table 168.

Table 168. Composition of Wood^a
(per cent of dry weight)

	Redwood	Western Yellow Pine	Sugar Pine	Live Oak
Benzene extract	0.34	2.22	2.84	0.52
Alcohol extract	4.39	1.49	1.90	4.52
Soluble in cold 5% NaOH	—	—	—	19.53
Soluble in cold water	—	—	—	3.82
Cellulose	54.89	57.72	59.18	47.47
Lignin	34.50	29.47	29.50	21.14
Pentosans not otherwise accounted for	3.67	3.49	1.86	1.97
Mannan	3.21	6.37	6.63	0.00
Galactan	0.50	0.78	0.50	1.56
	101.50	101.54	102.41	100.53

In general, some 50–60 per cent of dried wood is cellulose, about 20–30 per cent is lignin, and the remainder is composed of alkali-soluble hemicelluloses, natural resins, tannins, fats, proteins, and small amounts of other substances.

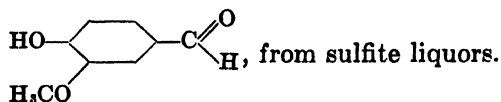
The fibrous structure of wood is afforded by its cellulosic content, while lignin, chiefly located in the secondary wall and partly in the middle lamella, binds the cells together. It is not known in what form lignin occurs naturally, for all processes which separate it from cellulose are sufficiently drastic in their action to cause some chemical alteration. It may be combined with carbohydrates in some glycosidic manner.

The chemical structure of lignin is still largely a matter of conjecture. Adding difficulty to constitutional problems is the fact that lignin varies according to source. Hard- and soft-wood lignins, for example, show distinct differences, so that they are probably not a single chemical species. Furthermore, it is likely that lignin from a given source is a mixture of several similar materials. Certain characteristic lignin reactions have, however, been clarified sufficiently so that a partial elucidation of its structure has been made. Lignin is composed of carbon, hydrogen, and oxygen, its carbon content varies between 62.4 and 64.3 per cent; its hydrogen content, from 5.4 to 6.1.

Essentially, it appears to be composed of a number of C_9 groups linked together through oxygen bridges and, possibly, carbon-to-carbon bonds to form a unit having a molecular weight of at least 840. Each of these C_9 groups possesses the carbon skeleton of *n*-propylbenzene and contains substituent oxygen groups in both side chain and nucleus. Nuclear substitution is *meta* and *para* to the C_3 side chain. The presence of methoxyl groups is characteristic of lignin, their content ranging from 14 to 21 per cent according to source. Indeed, methanol obtained by wood distillation is reported to be derived exclusively from lignin. The methoxyl radicals,

of which there appear to be four in each 840 unit, are meta to the C_3 side chains. Oxygen bridges or phenolic hydroxyls are para to the side chains. Each 840 unit appears to possess at least one free phenolic group. In every 840 unit there are also three or four other non-phenolic hydroxyl groups which appear to be attached to the side chains. One of them is enolic.

The presence in lignin of the aromatic groups mentioned above permits industrial preparation of vanillin,



Destructive distillation of recovered lignin has been said to offer a source of tar richer in phenol and its homologs than coal tar, although this operation has not yet been commercialized.

Catalytic and high pressure hydrogenation of lignin yields a liquid product which may serve as a source of various chemicals, including propylcyclohexane and various hydroxylated derivatives thereof, should a demand for these compounds arise.

The hydroxyl groups of alkali lignin can be esterified with acid chlorides. Various esters have been prepared in this manner, but industrial uses for them do not appear to have been developed yet.

Various color reactions have been proposed as a means of detecting lignin. Best known is the phloroglucinol reaction whereby a bright purple color is produced on spotting a lignin-containing material with a solution of phloroglucinol in concentrated hydrochloric acid. Whether or not this color is actually caused by lignin or by other substances associated therewith is still a matter of dispute. In any event, lignin plastics derived from sulfite liquors do not give this color reaction, so that it is not reliable as a general means of identification. Methoxyl determination appears to be the only reasonably satisfactory method for detection and estimation of these resins. In such analyses the presence of wood flour or other lignin-bearing fillers must be discounted.

Several excellent reviews of the present status of the structure of lignin have been published and are listed in the references at the end of this chapter. They should be consulted for further details.

Isolation of Lignin. Lignin may be separated from the cellulosic components of wood by three general methods, namely:

(1) Hydrolysis of the cellulose to soluble carbohydrates by means of strong mineral acids, leaving lignin behind as an insoluble residue. This process, which is utilized industrially in Europe for the manufacture of wood sugar, yields so-called "acid lignin." Commercialization in the

United States has been proposed, but is not yet a fact. (A comprehensive symposium on "Sugars from Wood" appeared in *Ind. Eng. Chem.*, 37, 4-54 (1945).) Few commercialized plastics applications of acid lignin are yet known. Certain plastics from bagasse and coffee may perhaps fall in this group.

A separational process similar in principle to the hydrolytic method was developed by Freudenberg, using cuprammonium solution to dissolve out the cellulose after preliminary hydrolysis with dilute acid.

(2) Solution of the lignin by heating with an organic solvent—often hydroxylated, in the presence of a catalyst such as ferric chloride or hydrochloric acid. The cellulose is left behind, in this instance, as an insoluble residue. Some of the solvent used reacts with the lignin during this treatment and the product is named according to the extractant employed, for example methanol lignin, butanol lignin, glycol lignin, phenol lignin, etc. Alcohol lignins are not commercial products. Some more or less experimental bagasse plastics appear to belong to this general category.

(3) Extraction of lignin from cellulose in aqueous solution by treatment with various inorganic reagents. This general procedure is very widely used by the three principal methods of paper making: the sulfite, sulfate, and soda processes.

In sulfite mills, wood chips are digested at elevated temperature with acid sulfites of calcium, magnesium, or sodium. The lignin is leached away from the cellulose and passes into solution as a salt of ligno-sulfonic acid.

In the sulfate or kraft process, wood chips are digested at elevated temperature with a five per cent solution of sodium sulfide and sodium hydroxide in the ratio of 1:2. The lignin passes into solution as a mixture of thiolignin and alkali lignin.

In the soda process, the lignin is dissolved away from the cellulose by treatment with caustic soda at high temperatures and passes into solution as alkali lignin.

Plastics from Waste Sulfite Liquors

The Marathon Corporation has pioneered in the manufacture of lignin plastics. Their source of lignin is waste sulfite liquor treated according to the Marathon-Howard process to precipitate lignosulfonic acid as a basic calcium salt.

Waste sulfite liquor contains dissolved sulfur dioxide—both free and organically bound, lignosulfonic acid, and carbohydrates. The Marathon-Howard process makes use of fractional precipitation by means of calcium hydroxide. Fractionation is carried out in three steps, each of

which is followed by settling and decanting or filtering. Recourse is not had to evaporation and both dilute and concentrated liquors can be handled in the process. In the first operation, milk of lime is added to precipitate free and loosely organically combined sulfur dioxide. Although a small amount of organic matter is brought down simultaneously, it is relatively slight and the sludge, which is essentially precipitated calcium sulfite, is returned to the pulping operations where it is used to make fresh cooking acid. The pH of the decant from this first operation is about 10.5. Lignosulfonic acid salts and carbohydrates are left in solution. A second liming operation is carried out until the pH is raised to above 12, whereupon most of the lignin is precipitated as a basic calcium lignosulfonate. The organic product is filtered off and further treated for various purposes, including plastics manufacture as described below. The filtrate is again limed to remove residual lignosulfonic acid. The precipitate from this final treatment contains a small amount of organic matter mixed with large quantities of lime. It is returned as a sludge to the initial recovery operation where it is used as precipitant. Its lignin content is thus recycled and recovered during subsequent treatments. The overflow, containing principally modified carbohydrates, is discarded. It is markedly improved over the original waste sulfite liquor from the point of view of stream pollution.

The organic product, obtained as the result of the second liming operation in this process, amounts to about half of the initial organic content of the waste liquor and contains principally basic calcium lignosulfonate. It may be utilized in several ways among which the most obvious is for a boiler fuel in plant operations. This use is economically feasible only in those locations where fuel is expensive and cost of lime is low.

More judicious applications result from treatment of its aqueous solutions at a pH of less than 10, with salts of magnesium, sodium, or other metals. By double decomposition, such salts as the sulfates precipitate inorganic calcium compounds and leave behind aqueous solutions of magnesium, sodium, or other metal salts of lignosulfonic acid.

Numerous salts can be prepared in this manner by varying not only metal, but also by controlling the hydrogen ion concentration during metathesis.

With the exception of the basic calcium and lead salts, most of the lignosulfonates disperse in water to yield colloidal solutions under all pH conditions. The basic calcium salt can be dissolved in water under neutral or acid conditions. All of these salts are insoluble in most organic solvents.

Numerous uses for these lignosulfonates have been proposed and some of them have attained considerable industrial importance within recent years.

Of special significance to the plastics industry is the treatment of the organic precipitate (from the second liming operation) by cooking with caustic soda under 175 pounds steam pressure, whereby it is chemically altered. Vanillin and certain other identifiable organic compounds are produced, while at the same time much of the lignosulfonic acid is partially desulfonated and converted to a sodium salt of a more or less resinous acid which contains about one-third as much sulfur as the original product. The digested liquor is extracted with butyl alcohol to dissolve the vanillin, which is then processed further.

By mineral acid precipitation of the aqueous solution remaining behind from butanol extraction, the sodium salt of partially desulfonated lignosulfonic acid is precipitated. It is soluble in both alcohols and phenols and can be used as an extender for phenolic resins in molding powders and laminating varnishes in amounts up to 50 per cent of the phenolic solids. It has enjoyed commercial use for this purpose to a limited extent, especially during the acute phenol shortage following Pearl Harbor. It may be incorporated with the phenolic resin either during manufacture of the latter or at a later stage. If introduced with the initial reactants, a somewhat larger amount of formaldehyde is required than would normally be used because some reaction occurs therewith. Moreover, because of its slight acidity and buffering effect, a slightly larger amount of alkaline catalyst is required to bring about proper condensation.

The merit of this material as an extender for phenolic resins is still a matter of opinion. Some manufacturers claim that its use detracts from the physical properties of the finished plastics, especially with respect to water resistance. The extent of this unfavorable behavior is uncertain.

More useful plastics are obtained from the alkali digested liquor, by further digestion with wood chips. By this process, sufficient organic acids are liberated on hydrolysis of the wood to precipitate a lignin derivative upon the cellulosic fibers which can then be defibrated and sheeted on standard paper-making machinery. The brown sheets of lignin-enriched paper thus obtained can be stacked and laminated under heat and pressure in much the same manner as phenolic laminates are produced. Sheets used for laminating contain from 35 to 45 per cent lignin resin. Without addition of phenolic resin, but when suitably moistened with water or a plasticizing agent, the lignin content of these



Courtesy Marathon Corp.

Figure 307. Dumping of the rotary digester used in making lignin-enriched chips. The stage illustrated here is followed by mechanical defibration, screening, washing, and lapping on a regular pulp wet machine.



Courtesy Marathon Corp.

Figure 308. Sawing a two-inch slab of "Lignolite."

sheets is thermoplastic. Upon laminating, curing does not occur and the cycles may be relatively short. In order to avoid driving out the plasticizing water during lamination, full pressure is applied before the platens are heated. Because of their thermoplastic character, lignin laminates of this type may be hot-formed.

Laminated lignin plastics are made by the Marathon Corporation under the trade-mark "Lignolite." They are available in natural black satin-finish or molded sandblast surfaces. By use of phenolic, urea, or melamine top sheets, these lignin plastics can be varied in color and in surface design. They may also be covered with various resin coatings.

These laminates are easily machined. They are resistant to water, oil, grease, and dilute acids. They should not be used above 80°, for above this temperature, they tend to blister and delaminate. Physical and electrical properties are listed in Table 169. Electrical characteristics, in particular, are unusually good for this type of plastic.

Table 169. Physical and Electrical Properties of "Lignolite," Grade 130 *, †

Specific Gravity	1.40
Specific Volume	20.5 cu in per lb
Tensile Strength	7,500–12,000 lbs per sq in
Compressive Strength	25,000–35,000 lbs per sq in
Flexural Strength—Edgewise	16,000–20,000 lbs sq in
—Flatwise	16,000–20,000 lbs per sq in
Impact Strength	1.27–1.50 ft lbs per in of notch (Izod)
Surface Hardness	104 Rockwell M 40 Brinell
Maximum Heat Resistance	4 hrs: 80° (176° F) Continuous: 70° (160° F)
Moisture Absorption—24 Hour Immersion	
Thickness in Inches	
$\frac{1}{16}$	4–5%
$\frac{1}{8}$	3.0%–4.0%
$\frac{1}{4}$	1.5%
$\frac{1}{2}$	0.70%
Dielectric Strength—Short Time Test	
Thickness in Inches	
$\frac{1}{16}$	700–900 volts per mil
$\frac{1}{8}$	550–700 volts per mil
$\frac{1}{4}$	500–700 volts per mil
Dielectric Strength—Step by Step Test	
Thickness in Inches	
$\frac{1}{16}$	450–650 volts per mil
$\frac{1}{8}$	550–600 volts per mil
$\frac{1}{4}$	350–500 volts per mil
Dielectric Constant	5.0
Power Factor	0.035
Loss Factor	0.175
Arc Resistance	183–188 seconds

* Manufacturers' data. Marathon Corporation, Chemical Division.

† These tests were made in accordance with accepted A.S.T.M. Methods.

Among the most important uses of lignin laminates are foundry pattern plates, plate sets for punching sheet metal, and switchboard and other electrical applications. Numerous uses have been made in the hardware and furniture fields.

Lignin enriched paper sheets may be reinforced with 10 to 30 per cent phenolic resin by surface application of varnish to one side of the sheets or by impregnation before laminating. Improved water and heat resistance as well as uniform surface appearance can thus be obtained. Marked improvement of arc resistance over that of standard phenolic laminates is shown by plastics of this type. They exhibit an arc resistance of 150 seconds, for example, as compared with 5-10 seconds for typical phenolic laminates. Other properties are shown in Table 170.

Table 170. Properties of Marathon Lignin Laminate "Lignolite," Grade 230 Series *

Flexural Strength	10,200-13,320 lbs per sq in
Impact Strength	
Flatwise	0.61-0.73 ft lbs per inch of notch (Izod)
Edgewise	0.31-0.37 ft lbs per inch of notch (Izod)
Water Absorption	
$\frac{1}{2}$ " Thickness	0.39
$\frac{1}{4}$ " "	0.72
$\frac{1}{8}$ " "	1.00
$\frac{1}{16}$ " "	3.00
Bonding	810-848
Heat Resistance	115° (continuous) (246° F)
Arc Resistance	157 seconds
Dielectric Constant	5.20
Power Factor	0.034
Dielectric Strength	
Step-by-Step $\frac{1}{8}$ "	530 v per mil
Short Time $\frac{1}{8}$ "	640 v per mil

* Manufacturers' data. Marathon Corporation, Chemical Division.

The lignin-enriched pulp, used as the starting point in the manufacture of lignin sheets for laminating, may also be washed, dried, and ground to give a lignin enriched filler. Molding compositions may be made by incorporation of as much as 80 parts of this material with 20 parts of phenolic resin. Even lower amounts of phenolic resin may be employed, but only by sacrificing flow characteristics.

Impact resistance is from 50 to 150 per cent higher than that shown by general purpose wood-flour filled phenolics. Good electrical properties are maintained.

Physical tests carried out at the Bureau of Standards upon molded samples of a lignin plastic reported to contain 23 per cent phenolic resin and 77 per cent lignin material of this type, together with about 1

per cent of metal stearates as lubricant gave the results listed in Table 171.

The molding of shaped articles from preforms of lignin-enriched pulp has been investigated, but is not yet practiced commercially.

Table 171. Properties of Molded Lignin-Phenolic Plastics¹

Specific gravity	1.37-1.44 lbs/sq in
Flexural strength	9240-10,940 lbs/sq in
Impact strength, Izod	0.28-0.43 ft-lbs/in of notch
Water absorption, 24 hrs (6 × 3 × ¼ in specimens)	
Weight increase	0.41-0.43 %
Dimensional increase	
Length	0.03-0.07 %
Width	0.00-0.07 %
Thickness	0.00-0.4 %

Plastics from Alkali Lignin

The soda and sulfate pulp processes have not offered so much incentive for recovery of by-product lignin as sulfite pulping, because economic operation of these paper-making methods depends on burning the wastes for their fuel value and for recovery and recycling of alkali. Stream pollution is therefore not encountered. Nevertheless, attempts have been made in a small way to derive profitable lignin products from the liquors of these processes.

Alkali lignin can be recovered from the liquors of both soda and sulfate processes by precipitation with carbon dioxide. A material known as "Meadol" is obtained in this manner, as a by-product of the soda process, by the Mead Corporation. In its manufacture, the gravity of the soda black liquor is adjusted to 1.10, thereby assuring 19 per cent solids content, of which three-fifths is organic and the remainder inorganic, chiefly sodium carbonate. Carbon dioxide is passed through the liquor in a closed tank of 2000 gallon capacity, about 8 to 9 hours being required for completion of precipitation; at the end of this time the pH reaches a value of 8.3 to 8.5. The alkali lignin is thrown out of solution in such a fine state of subdivision that it must be heated to 90°, then cooled immediately to 40°, with agitation, in order to permit filtration.

The filtrate, containing the soda and about 70 per cent of its original organic solids content, is evaporated and incinerated for recovery of soda ash. The filter cake is blown out, washed with water, dilute sulfuric acid, and again with water. It is then blown once more, dried on a double drum drier, and pulverized.

The moisture content of "Meadol" is 2-4 per cent; its ash averages 1.0-1.3 per cent. It melts between 210 and 235°, or much lower in the

presence of appreciable quantities of moisture. Unlike the lignosulfonates recovered from the sulfite process, this alkali lignin is insoluble in water and dilute mineral acids. It is soluble in dilute alkalies and in polar organic solvents, including organic acids, alcohols, and amines. It is insoluble in non-polar solvents such as petroleum naphthas.

Alkali lignin has been used in small measure as an extender for phenolic resins, but the properties of the plastics thus produced are inferior to those of standard phenolic resins. It can also be used directly as a binder for fibrous fillers, but such products do not now appear to be manufactured. Outside of the plastics field, an interesting use of "Meadol" is as expander in the negative plate of storage batteries.

Numerous esters of "Meadol" have been prepared, using acid chlorides as reagent. The lower aliphatic acids yield penta derivatives, the intermediate ones give tetra esters, while palmitic and stearic acids esterify only three hydroxyl groups per lignin unit. These products have not yet attained any commercial importance, although use of the stearate as a mold lubricant and component of printing inks has been suggested. Dibasic acids yield resinous products for which no use has been reported.

The West Virginia Pulp and Paper Company has also produced small amounts of alkali lignin as a by-product from its sulfate pulping process.

Plastics from Exploded Wood Chips

For a few years following 1937, the Masonite Corporation manufactured lignin plastics under the trade-mark "Benalite" and uncured lignin sheets for laminating under the name "Benaloid." The development of these products was an outgrowth of their earlier production of "Masonite" building board by explosion of wood chips and rebonding under simultaneous application of heat and pressure. By careful control of reaction conditions, it was found possible to convert all of the wood to a plastic condition which could be remolded.

The operation used in the production of these lignin plastics consisted of charging guns of twelve cubic feet capacity with wood chips and treating the charge with live steam at 1200 lbs per sq in during a few seconds. This steam treatment caused acid-hydrolysis of the woody components because of the formation of formic and acetic acids by decomposition of the wood. Hydrolysis resulted in activation of the lignin so that it could serve as a resinous bond for the residual cellulosic fibers. The hemicellulosic content of the wood was largely hydrolyzed to soluble sugars which were later removed, while the cellulose was scarcely altered chemically. After hydrolysis by super-heated steam had proceeded for a

sufficient length of time, the pressure was suddenly released and the hydrolyzed chips exploded as a result of the high internal pressure. Careful control of the cycle was necessary. Changes of a fraction of a second produced perceptible alteration in the properties of the product and a second might differentiate between success and failure. The complete round of charging the guns, steam-treating, exploding, and emptying required approximately one minute.

The product from this treatment was a mass of cellulosic fibers coated with activated lignin. The hydrolyzed hemicelluloses were washed out and the fibrous material worked up into heavy brown sheets on paper-making machinery. These lignin sheets were then laminated under heat and pressure in much the same manner as phenolic laminates. Indeed, the activated lignin produced by this method of manufacture appeared to possess certain characteristics of thermosetting resins, for once cured, "Benalite" could not be disintegrated and remolded. Molding was carried out at 175° and 1500 lbs per sq in pressure in the presence of about 4 per cent moisture as plasticizer.

Because of the necessity of utilizing manufacturing equipment for certain products of a critical military nature, commercial "Benalite" operations ceased during World War II. Properties of the pre-war plastic are not listed here because it is said that they cannot be considered characteristic of future developments in this field.

Plastics from Bagasse

Following up work reported in 1931 by the Color and Farm Waste Division of the Bureau of Chemistry and Soils in Washington, the U. S. Forest Products Laboratory in Wisconsin has carried out extensive study of lignin plastics derived from wood by treatment with hydrochloric acid and by reaction and plasticization with phenols, aromatic amines, and furfural accompanied by digestion in the presence of steam.

With these studies as a foundation, the Agricultural By-Products Laboratory at Ames, Iowa, applied similar methods of treatment to bagasse, obtaining promising results in the preparation of molding powders.

Dry bagasse contains about 18 per cent lignin, 45 per cent cellulose, and 15 per cent water extractives. The balance is composed mostly of hemicelluloses. Study of the preparation of lignin plastics by digestion with aniline under heat and pressure, in the presence of water, showed the following facts:

- (1) The amount of aniline employed should be from one-fifth to one-fourth the weight of dry bagasse.

- (2) Incomplete digestion results in production of molding powders

which stick in the mold. Digestion times of at least three hours cause complete hydrolysis of the materials responsible for sticking.

(3) The amount of water used is reflected in the physical properties of the resultant plastic. A high water-to-bagasse ratio yields maximum strength, but low flow and poor water resistance.

(4) Digestion pressures also exercise an influence upon the physical properties of the product. They should be low for maximum strength, but high for maximum flow and water resistance.

To date, the only commercial venture attempting to utilize these processes appears to be that of Valentine Sugars in Lockport, La. This company has obtained licenses to operate under the public service patents of the Forest Products Laboratory and is producing thermosetting lignin plastics on a developmental scale from bagasse under the trade name "Valite." Many shortcomings of both powder and molded plastic were first encountered, leading to evolution of a molding powder produced by combining two different bagasse products—one a filler, the other a resin—and then mixing them in suitable proportions. The bagasse filler is said to impart better properties to this resin than does wood flour, although it cannot be used satisfactorily in place of the latter with phenolic resins. Good flow, short curing time, absence of gassing, and good strength characteristics have thus been obtained. Molding compounds have been developed which, in 1/8 inch thickness, can be cured in one minute at 300–350° F under 2000 lbs or more per sq in.

These products are somewhat soft and flexible immediately after curing and are said to be especially suitable for molding screw caps or other articles where stripping from an undercut mold is desirable. This post-cure flexibility does not cause distortion of the molded piece, nor does it reappear upon heating again to temperatures even as high as 400° F.

"Valite" is still in the developmental stage. Standardization upon one or more specific resins has not occurred, hence no exact physical properties for commercial products can be quoted. Nevertheless, the characteristics given in Table 172, indicative of the properties to be expected, have been published for four different experimental products of this general type.

Other bagasse plastic developments include a laminating resin and a developmental thermoplastic molding compound.

Redwood Plastics

Redwood contains a particularly large proportion of alcohol- and benzene-soluble phlobaphenes and other materials. Table 173 shows the total extractives in redwood, according to source.

Table 172.¹⁵ Physical Properties and Characteristics of Four Typical Bagasse Plastic Compounds^a

Compound	A	B	C	D
Molding quality	Excellent	Excellent	Good	Good
Molding temperature, ° F	300-350	300-350	300-375	300-375
Molding pressure, psi	2000-3000	2000-3000	2000-10,000	2000-10,000
Compression ratio	2.5	2.5	3.0	3.0
Specific gravity	1.35-1.40	1.35-1.40	1.30-1.40	1.30-1.45
Flexural strength, psi	8900	9500	10,100	9500
Impact strength, unnotched Izod, ft-lb, $\frac{1}{2}$ in \times $\frac{1}{2}$ in bar	1.10	1.00	1.39	1.25
Resistance to heat, ° F	350	380	400	400
Dielectric strength, volts per mil, step	250	— ^b	— ^b	— ^b
Water absorption 48 hr, per cent	0.90	0.75	— ^b	— ^b
Burning rate	Very low	Very low	Very low	Very low
Effect of age	Apparently none			
Effect of weak acids	Slight			
Effect of alkalis	Slight surface roughening, 168 hr boiling with 25% sodium hydroxide			
Effect of organic solvents	None, to a slight surface roughening			
Effect on metal	Inert	Inert	Inert	Inert
Colors	Dark	Dark	Dark	Dark

^a Due to the limited amount of commercial experience with these materials, only limited laboratory results are available. Data given above should only be considered as indicative of the properties of these materials and not taken as a guarantee of performance.

^b No data available.

Table 173. Relative Amounts of Extractives in Redwood ¹¹

	Extractives	Residue
Heartwood	10.2	89.8
Stumps	20.1	79.9
Roots	32.3	67.7

From 34 to 38 per cent of the residue is lignin, from 52 to 56 per cent is cellulose, while the remainder is chiefly hemicellulosic.

The Pacific Lumber Co. of Scotia, California, has undertaken a long-term investigation of redwood waste conservation at the Institute of Paper Chemistry. As a result of these studies, it has been found possible to produce several different types of plastics from redwood.

The flour itself can be molded without any addition or alteration, for it is thermoplastic in nature. The greater the extractive content, the better the moldability. Flow is poor at best, and pressures of at least 5000 lbs per sq in must be employed at temperatures in the order of 320° F. Plasticizers such as glycerol or furfural improve flow, while a certain degree of water repellency can be imparted to the product by incorporation of a hardener such as hexamethylene tetramine.

Redwood flour may also be used as a filler in large amounts with phenolic resins. Ratios of 3 parts of flour to 1 part of resin yield powders which can be molded, but physical properties, especially water resistance, of the molded article are poor.

Redwood wastes may also be treated with steam, in somewhat the same manner as that used in making "Benalite," to yield a pulp which of itself can be molded and which is also capable of serving as a base for subsequent treatment in the production of plastics. The pulp itself is thermoplastic. If molded alone, therefore, molds must be cooled before ejection. The molded articles are sensitive to water vapor. They swell and become sticky in high humidities. Where admixed with 5 per cent of "Vinsol" or "Meadol," properties are somewhat improved.

Although none of the foregoing plastics are successful commercial articles, they pointed the way to development of thermosetting molding compounds by chemical modification of cooked redwood pulp. Details of the process have not been completely revealed. It is not improbable that it is based upon the work of the Forest Products Laboratory mentioned in the preceding section. Especially useful products can be obtained by admixture with certain furfural resins.

Two different thermosetting redwood plastics have appeared as commercial articles. "Shellerite," produced by the Sheller Manufacturing Corp., has been successfully used in large scale molding of steering wheels about a metal insert. "Colemorite," made by the Vulcanized

Rubber & Plastics Co., can be not only molded, but also tubed and calendered. The nature of the resinous binder utilized in "Colemorite" is discussed in Chapter 26.

Table 174 compares a few physical properties of different kinds of redwood plastics produced in the laboratories of the Institute of Paper Chemistry.

Physical properties of "Shellerite" and "Colemorite" are given in Tables 175 and 176.

Table 174. Comparison of Various Types of Redwood Plastics ¹¹

Type of Plastic	Tensile Strength lbs/sq in	Flexural Strength lbs/sq in	Impact Strength Unnotched Charpy ft lbs/in of width	Water Absorption 24 hrs (A.S.T.M. D570-42T)
Stumpwood flour, plasticized and hardened *	6,450	10,400	1.0	—
Stumpwood flour plus phenolic resin †	5,300	7,500	0.55-0.60	2.5
Cooked pulp, alone	5,480	7,700-8,000	0.58	2.5-3.0
Cooked pulp and alkali lignin ‡	6,700	8,000	0.45	2.0-2.5
Thermosetting pulp molding powder	5,000	6,500	0.37-0.40	1.0

* 91.5 pts. flour, 3 pts. glycerol, 5 pts. hexa, 0.5 pts. condensation black.

† 74 pts. flour, 25 pts. "Durez" 114, 0.5 pts. calcium stearate, 0.5 pts. carbon black.

‡ 95 pts. pulp, 5 pts. "Meadol."

Table 175. Properties of "Shellerite" *

Tensile strength	4700-4800 lbs/sq in
Flexural strength	6000-7000 lbs/sq in
Compressive strength	18,000-20,000 lbs/sq in
Impact strength, notched Izod, ft-lbs/in of notch	0.44-0.65
Rockwell hardness ¼ in ball, 60 kg load	B113-119

* Manufacturers' data. Sheller Manufacturing Corp.

Table 176. Physical and Chemical Properties of "Colemorite" *

	2-L	3B-F5
Molding Qualities	Excellent	Excellent
Compression Molding, Temperature, ° F	220-330	300-350
Compression Molding, Pressure, lbs per sq in	300-1000	2500-4000
Mold Shrinkage, inch per inch	0.0133	0.007-0.010
Specific Gravity	1.35	1.40
Specific Volume, cu in per lb	20.5	19.1
Tensile Strength, psi	5220	4500
% Elongation	1.61	1.40
Impact Strength (Izod), ft lbs energy	0.15	0.14-0.16
Rockwell Hardness, 60 kg, ¼" ball point	M85-M95	M95-M100
Tendency to Cold Flow	Nil	Nil

Table 176—(Continued)

	2-L	3B-F5
Water Absorption, immersion—24 hrs	0.0–0.5	—
Burning Rate	Nil	Nil
Effect of Age	None	None
Absorption in 1.30 Sulfuric Acid, 80° F, 28 days' immersion	0.52	—
Absorption in 1.30 Sulfuric Acid, 150° F, 23 days' immersion	2.8–2.9	—
Nitric Acid, Sp. Gr. 1.125, 16° B \acute{e} or 21.5%	Attacked	—
Hydrochloric Acid (conc.) Sp. Gr. 1.19	Attacks slightly	—
Hydrofluoric Acid (48% conc.), Absorption—24 hrs	3.30	—
Bromine Water, saturated, Absorption—24 hrs	1.53	—
Acetic Acid (glacial, 99.5%), Absorption—10 days	0.615	—
D-72 Developer, Absorption—240 hrs	0.39	—
Hypo Fixing Solution, Absorption—240 hrs	1.87	—
Effect of Weak Alkalies	None—Slight Depending on alkali	Slight
Effect of Strong Alkalies	Attacked badly	Attacked badly
Effect of Organic Solvents	None †	—
Effect on Metal Inserts	Inert	Inert
Machining Qualities	Good	Good
Clarity	Opaque	Opaque
Color Possibilities	Limited	Limited

* Manufacturers' data. The Vulcanized Rubber & Plastics Company.

† Ketones are absorbed rather rapidly but without apparent surface defects.

Coffee Plastics

During the past few years considerable publicity has been given to plastics derived from coffee beans. A plant has been erected in Brazil for conversion of surplus coffee crops into this new material, named "Caffelite." To date, this plastic has not appeared upon the American market and it is said that plant operations in Brazil have not yet been attended with much success.

A detailed analysis of Brazilian coffee beans has been reported as follows:

Table 177. Chemical Composition of Brazilian Coffee Beans ²⁷

Water	12.0	Reducing sugar	1.0
Fat	10.0	Sucrose	6.4
Soluble ash	3.2	Chlorogenic acid	5.7
Insoluble ash	0.1	Caffeic acid	0.7
Caffeine	1.0	Other water-solubles	6.0
Trigonelline	1.0	Alcohol extractives	2.5
Protein	12.9	Lignin	4.2
Cellulose	11.2	Hemicellulose	20.2

Because of the low lignin content, there may be some question as to whether or not these plastics should be classified as lignin products. Processing operations, however, remove oil, caffeine, and water-solubles so that the lignin probably amounts to at least 17 per cent of the residue, a fact which would seem to indicate that basically "Caffelite" should be considered an acid lignin plastic.

The process of transforming coffee beans to "Caffelite" is essentially one of grinding, extracting oil and caffeine, hydrolyzing with water and an acid catalyst in an autoclave at 300° F, washing, neutralizing and drying the thermosetting molding powder which can then be compounded with lubricants, dyes, or other modifying additives.

Manufacture of tile and wallboard as well as molding powder is contemplated.

Lignin Plastics from Miscellaneous Wastes

Much work has been done on the conversion of other wastes to plastics. Various nutshells, hulls, straw, corncobs, palmetto roots, etc. have been studied, but as yet there appear to be no commercial lignin plastics produced from these agricultural by-products, despite their availability in very large quantities.

The approximate lignin content of a number of dried waste materials is indicated in Table 178.

Table 178. Approximate Percentage Composition of Various Plant Materials ^{14, 17}

Material *	Cellulose (%)	Lignin (%)	Pentosans (%)
Bagasse	60	22	29
Cornstalks	38	34	28
Corncobs	71	19	32
Barley straw	49	16	32
Oat straw	44	19	23
Rice straw	46	11	22
Rye straw	36	11	20
Seed flax straw	65	22	20
Wheat straw	57	7	28
Jerusalem artichoke tops	—	12	15
Jute	75	12	18
Hemp	79	5	6

* Considerable disagreement exists between various authors in the cases of some of these products.

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Chapter 24

Protein Plastics

General

All proteins are extremely complex high molecular weight condensation products of α -amino acids. In a certain sense, therefore, they may be considered as natural plastics. Most of them, however, are far more useful as foodstuffs than as fabricated articles. Few will deny that a juicy beefsteak, for example, is infinitely more enticing than the most artistic button or buckle! Nevertheless, since the appearance of certain agricultural surpluses following World War I, there has been considerable activity in the development of semi-synthetic plastics from a few proteinaceous substances. Thus far investigations have been confined largely to proteins derived from skim-milk, soybeans, and corn. Industrial use of casein is very definitely limited by the amount of skim-milk available as a by-product in excess of food requirements. In the case of zein, production is again of a by-product nature, for it is derived from gluten residues resulting from corn starch manufacture. Although far from developed to their fullest extent, soybeans appear to offer the greatest potential source of industrial protein. They can be grown in unlimited quantities and contain approximately 40 per cent protein.

Numerous other proteinaceous materials have been studied less intensively, both here and abroad, as sources of semi-synthetic plastics, but are of little significance today. Related substances like keratin from horny substances and even chicken feathers have received some attention. Fabrics from the latter material and also from peanut protein are being produced on a developmental scale in this country.

One of the earliest successful semi-synthetic plastics—antedated only by "Celluloid"—was developed from casein in 1898 during the course of an attempt to produce white slates for German school children. The product, known as "Galalith" from the Greek meaning "milk stone," has enjoyed much popularity in Europe for innumerable applications, although offspring of the master race continued to use white chalk on gray slates for many years despite its discovery. The more rigorous climatic conditions of the United States have limited applications of this plastic to ornamental buttons, buckles, and costume jewelry, for

casein plastics are prone to develop surface cracks in an atmosphere of fluctuating humidity.

Soybean protein is a much more recent article of commerce. Although the newspapers have led the public to believe that plastic automobiles from soybeans are just around the corner, the utility of this protein in molded plastics at present is, in fact, almost negligible.

Zein, from corn, is a prolamine and therefore unique in many of its properties. It yields plastics which are aggravatingly close to desirable products, but this newcomer to the ranks of commercial proteins has thus far insisted upon retaining the undesirable characteristic of all other protein plastics—lack of water resistance.

All three of these commercial proteins have found important uses in adhesives, paints, sizes, emulsifying agents, and extruded filaments. In most of these applications, full utility of the protein is developed only by hardening with formaldehyde or some other chemical. The production of plastics and allied materials from these proteins thus falls in the same category as the formation of water-insoluble glues from animal gelatin or isinglass and the tanning of hides to yield leather.

Despite the considerable amount of research which has been expended upon these proteins, they are still relatively unimportant in the field of molded plastics, especially insofar as industrial applications are concerned. For the purposes of this text, therefore, a very brief and elementary review of their present status will suffice.

Casein Plastics

Casein occurs in cows' milk to the extent of some 3 per cent, being present in the form of calcium caseinate. It is separated from skim-milk, a process which can be carried out in several ways. Commercial methods involve either precipitation by an acid at the isoelectric point (pH 4.6–4.7), or coagulation by rennin—extracted from the inner lining of the fourth stomach of young calves and lambs. The bulk of this protein is obtained by acid precipitation and finds its way into adhesives, fibers, paints, and coatings for paper and leather. In the manufacture of current plastics, only material prepared by the use of rennin and distinguished by an appreciable ash content—not less than 7.5 per cent—is suitable. Moreover, the skim-milk so treated must be fresh, for if slightly soured the acid content is sufficient to detract appreciably from the merit of plastics produced from the coagulum.

The structure of casein, like that of all other proteins, is as yet unknown. Its molecular weight has been estimated variously between 12,800 and 192,000. It contains free amino groups and is composed of α -amino acids in the approximate proportions shown in Table 179.

Table 179. Approximate Percentage of Amino Acids in Milk Proteins *
(Calculated to 16.0 Per Cent Nitrogen)

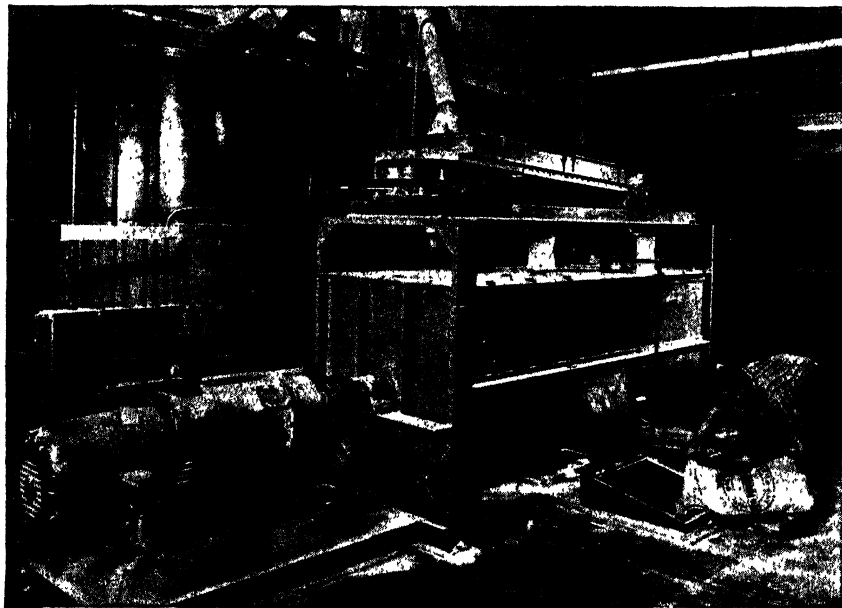
Amino Acids	Casein	Lactalbumin	β -Lacto-Globulin	Whole Milk Cow	Whole Milk Human*
Arginine	4.1 \pm 0.2	3.5 \pm 0.5	3.1	4.3	5.0
Histidine	2.5 \pm 0.3	2.0 \pm 0.3	1.8	2.5	2.7
Lysine	6.9 \pm 0.7	8.0 \pm 1.1	10.4	7.5	7.2
Tyrosine	6.4 \pm 0.4	5.3 \pm 0.1	4.3	5.3	5.1
Tryptophane	1.8 \pm 0.2	2.3 \pm 0.3	2.0	1.6	1.9
Phenylalanine	5.2 \pm 0.5	5.6	5.3	5.7	5.9
Cystine	0.36 \pm 0.04	3.0 \pm 0.2	3.6	1.2	3.4
Methionine	3.5 \pm 0.3	2.8 \pm 0.2	3.6	2.8	2.0
Serine	6-7	4.9			
Threonine	3.9 \pm 0.1	5.3	6.0	4.6	4.6
Leucine	12.1	15	17.7 \pm 4.2		12.1 \pm 3.9
Isoleucine	6.5		6.6 \pm 0.6		5.2 \pm 0.3
Valine	7.0	4	7.9 \pm 1.4		5.5 \pm 1.5
Glutamic Acid	22.8		22.1		
Aspartic Acid	6.3		10.1		
Glycine	0.5				
Alanine	5.6	0-1			
Proline	8.2				
Hydroxyproline	2				

* Considered by Block and Bolling⁹ to represent the best balanced protein.

From the point of view of plastics manufacture, the essential reaction of casein is its ability to form an insoluble and hard material upon treatment with formaldehyde. When a small amount of water is present, commercial casein is thermoplastic; treatment with formaldehyde decreases its thermoplasticity. Numerous hypotheses have been advanced concerning the chemistry of the hardening reaction. Comparison of the properties of the initial and final products strongly suggests that cross-linking of linear chains occurs through introduction of methylene bridges.

One of the earliest methods of manufacturing casein plastics, the so-called "wet" process, involved dispersion of acid-precipitated casein in alkaline solution, addition of desired dyes or pigments, coagulation with an acid or acidic salt, compacting under about 500 lbs per sq in, and hardening by immersion in aqueous formaldehyde solution over a period of several weeks or months. Modifications of this method include (1) direct coagulation of an ammoniacal dispersion of casein with formaldehyde and (2) treatment of an alkaline suspension of casein with acetaldehyde and an organic acid. Wet processes are no longer used in the production of solid plastics, but are essentially the basis of methods used in the fabrication of casein wool, in which an alkaline dispersion, admixed with such additives as carbon disulfide, is forced through a spinneret into an acid precipitating bath and is then simultaneously or subsequently treated with formaldehyde and other modifying agents.

Casein wool was first produced in Italy in 1936 under the trade name "Lanital" (Italian wool) by Snia Viscosa. Numerous plants for the production of "Lanital" under this and other names have been erected in several countries. In the United States, Whittier and Gould, chemists of the Department of Agriculture, developed a similar process independently, differing in details, at about the time that "Lanital" first appeared. Casein wool, developed by F. C. Atwood, is now produced in



Courtesy Aralac, Inc.

Figure 309. In the manufacture of "Aralac," ground casein is poured into the trap-door, thoroughly mixed in the machine in the foreground, treated with chemicals and heated in huge vats, left background.

the United States, under the trade name "Aralac," in excess of five million pounds a year.

Casein wool has been widely used in blankets and clothing, especially in admixture with wool, and is said to have proved invaluable to the Italian army. In this country it has been employed not only in fabrics, but as a substitute for rabbits' fur in felt. It can be dyed with the customary wool (acid) dyestuffs and is markedly inferior to real wool only in wet strength, a property which has already been ameliorated and which will probably be further improved.

The manufacture of solid casein plastics is today carried out according to the so-called "dry" process by admixing rennet casein with some

30 to 40 per cent of water, together with suitable dyes, pigments, or color lakes, and extruding it with heat through a screw-type press in the shape of rods or tubes. By suitable use of pigments and by proper control of the introduction of colored slugs into the hopper of the extruder, brilliant colors and striking color combinations, including beautiful marbled and tortoise-shell effects, may be obtained. If a sheet is desired, extruded rods are laid against each other and flattened in an hydraulic press. The



Courtesy Aralac, Inc.

Figure 310. Concealed under the foam are four spinnerets. The four taffy-like strips are "Aralac" fibers in one of the first stages of processing. The hand indicates relative size. The fiber undergoes many other processes before it is ready for market.

resulting shapes are then cured by immersion in 4-5 per cent formaldehyde solution over a period ranging from a few days to several months, depending upon thickness. After the formaldehyde has been given an opportunity to react completely, the treated articles are removed from the bath, seasoned to allow evaporation of water, and finally straightened if necessary between steam-heated platens under relatively low pressure. Casein sheets, rods, and tubes may be readily machined and fabricated into buttons, buckles, and ornamental jewelry. The finished plastic may be buffed to a smooth surface, but a more permanent and less ex-

pensive gloss can be imparted by immersion in sodium or calcium hypochlorite solution.

In 1929, it was found that moistened casein, admixed with about 2 per cent of alum, could not only be extruded readily, but could also be

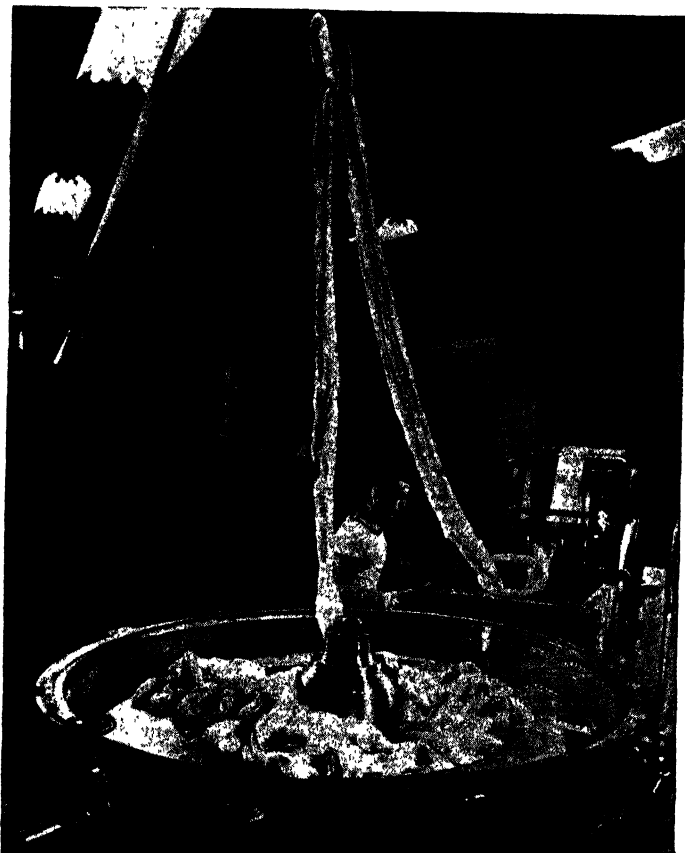


Courtesy Aralac, Inc.

Figure 311. This is an unretouched photograph of "Aralac" fiber as it comes out of the spinneret. This action was simulated in a specially prepared glass case using a more transparent solution than normally, in order to reveal the operation. Liquefied casein enters the spinneret through the pipe, lower left, and under pressure is forced through thousands of holes in the spinneret. The white "tape" at the top actually contains thousands of strands of fiber.

machined easily and even molded before hardening. Following this discovery, most of the casein plastics manufacturers in this country were consolidated with button producers and casein-alum mixtures are now extruded into rods and subsequently handled by (1) turning to shape on automatic machines and hardening; (2) slicing into preforms, hardening and turning; or (3) molding or punching in a hot mold and then

hardening. The final operation in any case involves polishing in hypochlorite solution at about 90°. Because of the relatively thin cross-section of the buttons produced by any one of the processes just mentioned, only a few days are required to complete hardening and the entire period of fabrication usually amounts to less than a week.



Courtesy Aralac, Inc.

Figure 312. In this apparatus, resembling a huge washing machine, chemicals used in the manufacture of "Aralac" are recovered for re-use. At this stage, the "tow" is nearly ready for cutting into small lengths.

Although casein buttons are made by a number of companies, the quantity of casein plastics available in the form of sheets, rods and tubes is restrained. Domestic production appears to be confined almost entirely to the American Plastics Corporation, the trade-mark "Ameroid" being applied to their products.

To date, efforts to develop casein molding powders have been unsuccessful.

The most serious objection to casein plastics is their lack of water resistance. After six weeks' immersion, for example, they absorb about 30 per cent of their weight of water. Cracks appear as a result of exposure to fluctuating humidity and temperature, so that these plastics cannot



Courtesy Aralac, Inc.

Figure 313. From the revolving drum at the top, cut and finished "Aralac" fiber drops down, ready to be baled and shipped to textile mills and other users.

even be used for the manufacture of combs, an important continental application. Principal domestic uses are in costume jewelry, especially buttons and buckles. Typical physical properties are listed in Table 180.

For a discussion of the use of casein in adhesives, paper and leather coatings, water-dispersible paints, and miscellaneous applications, references at the end of this chapter should be consulted.

Soybean Protein

The soybean appears to have been introduced into the United States as early as 1804. Twenty-five years later a botanical record mentions its

Table 180. Properties of Casein Plastic ²⁸

Test	General Purpose
Moldability in Compression Molds	Poor
Forming Temperature, ° F	200
Specific Gravity	1.34
Machining Quality	Good
Thermal Coefficient of Expansion, Linear per ° C	$4.1-6.8 \times 10^{-5}$
Heat Distortion Point, ° F (A.S.T.M. D648-41T)	300
Heat Resistance, ° F	300-325
Water Absorption, 24 Hrs., % (A.S.T.M. D570-40T)	7-14
Resistance to Indoor Aging	Hardens slightly
Chemical Resistance	*
Dielectric Strength, Short Time, V/M	400-700
Dielectric Constant, 1,000,000 Cycles (A.S.T.M. D150-41T)	6.15-6.8
Power Factor, 1,000,000 Cycles (A.S.T.M. D150-41T)	0.052
Impact Strength, Izod, Milled Notch, ft lbs/in (A.S.T.M. D256-41T)	1.0
Compressive Strength, psi	27,000-53,000
Flexural Strength, psi	10,000-18,000
Tensile Strength, psi	10,000
Elongation at Failure, %	2.5
Modulus of Elasticity in Compression, psi	400,000
Modulus of Elasticity in Tension, psi	$5.1-5.7 \times 10^6$
Rockwell Hardness ($\frac{1}{16}$ " ball)	26-28.5
Brinell Hardness (2.5 mm ball—25 kg load)	23

* Resistant to weak acids and organic solvents

Softens when exposed to weak alkalies

Decomposes when exposed to strong acids or strong alkalies

growth in New England. Little attention was paid to the plant, however, until after 1900 when its investigation was taken up by a few progressive farmers and agricultural laboratories. Much of the credit for the present importance of the American crop goes to the pioneering efforts of W. J. Morse and his director, the late C. V. Piper, both of the Bureau of Plant Industry in Washington. United States cultivation of soybeans is now exceeded only by China and Manchuria, production having jumped from 4,947,000 bushels in 1924 to 106,712,000 bushels in 1941 and nearly 260,000,000 bushels during the war years.

Soybeans contain about 20 per cent of oil which finds its way into numerous industrial applications, including superior oil-modified alkyd resins. The oil may be obtained by mechanical expression, but this process is relatively inefficient for about one-quarter of the original oil remains behind in the residual meal which goes into cattle feed or fertilizer. The more effectual way of obtaining soybean oil involves flaking and extraction with a suitable solvent, usually commercial hexane. In this manner over 99 per cent of the oil is obtained, leaving a meal which can readily be used for further chemical processing.

Soybeans also contain approximately 40 per cent of protein. This remains behind in the meal after extraction of oil and, either purified or in the form of crude meal, is used in adhesives, water paints, plastics, and

other industrial applications. Soybean adhesives are now extensively employed in the manufacture of plywood from pine and fir—an application pioneered by I. F. Laucks.

Ground soybean meal may be used as a reactive filler in phenolic molding compounds. In this application, although wood flour is also added, the soybean meal permits a reduction in the amount of phenol, with attendant decrease in cost of plastic. The only publicized application of this kind has been in some of Henry Ford's molded automobile parts, especially gear shift knobs, in which the phenolic molding compound has been modified with about 25 per cent of soybean meal. 1937 consumption of soybean meal by Ford for this purpose was reported as about 156 tons.

Of considerable industrial interest at present from the point of view of water soluble paints and adhesives, and of great potential interest in the fields of plastics and synthetic fibers is purified soybean protein which can be obtained from the crude meal. The protein constitutes about 50 per cent of solvent extracted meal, the remainder being largely carbohydrate in nature. Essentially, the operations whereby soybean protein is removed and purified consist of treating the meal from hexane extraction with ten to twenty times its weight of water, adding an alkaline material, such as sodium sulfite (0.1%) or a combination of sodium sulfite and sodium hydroxide, to effect solution of the protein, centrifuging or otherwise separating the insoluble matter, and precipitating the protein by means of an acidic substance added in such amount that the ultimate pH is adjusted to about 4.5. The product is then filtered and dried. In each of these operations, temperature control is important. Moreover, soybean protein is discolored by contact with iron so that careful selection of materials of construction is essential.

It should, perhaps, be emphasized that in contrast to casein which is strictly a farm by-product available only in excess of food requirements, soybeans constitute a relatively inexpensive and unlimited source of protein for industrial use. Both the variety of the plant and, to a less extent, the composition of the soil exercise an influence upon the protein content of the bean.

Investigations by G. H. Brother and his associates at the U. S. Regional Soybean Industrial Products Laboratory have resulted in the interesting discovery that formaldehyde treatment of soybean meal or protein within the isoelectric range of the latter yields a hardened product which exhibits thermoplastic characteristics. It is also of much practical, as well as theoretical interest, that the water-absorption of hardened protein is a minimum when hardening occurs within the isoelectric range, as shown by Figure 314.

Hardening or tanning agents other than formaldehyde may be used for preparation of thermoplastic molding compounds from soybean protein, but are less satisfactory. (Acid casein can also be hardened to a thermoplastic material under conditions similar to those given for soybean protein. Rennet casein gives far less interesting properties from this point of view, while zein shows better thermoplastic characteristics without aldehyde treatment.)

The thermoplastic proteinaceous materials listed above are not satisfactory for commercial molding operations because they can be plas-

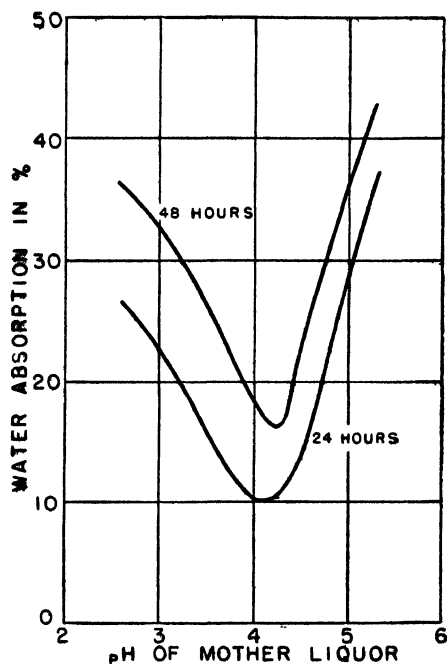


Figure 314. Variation in water absorption of hardened soybean protein with pH of hardening (Brother and McKinney¹⁴)

ticized properly only with water-soluble plasticizers. Thermoplastic formaldehyde-hardened soybean protein, however, can be incorporated mechanically with phenolic molding compounds in ratios ranging from $\frac{1}{4}$ to $\frac{3}{4}$, with or without added wood flour, to yield thermosetting molding powders showing excellent flow and other promising characteristics.

In addition to the uses mentioned above, soybean protein can be fabricated into a textile fiber in much the same manner as casein. In the spinning of soybean fibers, the slightly alkaline solution of protein is prepared under suitable conditions of time and temperature and then spun into an acid precipitating bath, usually sulfuric acid, containing formaldehyde and a mineral salt such as sodium chloride or aluminum

sulfate. The precipitated fiber is stretched in order to effect molecular orientation with consequent improvement of strength. It is then treated for a relatively long time in formaldehyde to set it completely, cut to appropriate staple length, and dried under carefully controlled atmospheric conditions.

Soybean fiber possesses a warm, soft feel and natural crimp. It exhibits only 80 per cent of the tensile strength of natural wool, but shows higher elongation when wet. It is less readily wetted than either natural wool or casein fiber. It is more resistant to moths than wool, and possesses a specific gravity of 1.31.

Ford operated a soybean protein fiber pilot plant for several years. The Drackett Company is now fabricating a similar material on a developmental scale. R. A. Boyer has pioneered both of these developments. One of the important uses foreseen for this material is in the manufacture of upholstery fabric, probably admixed with wool or other textiles.

Zein

Zein is the most recently available commercial protein. It is found only in corn gluten, a by-product of corn starch manufacture, and accounts for about 70 per cent of the proteins or 30 to 35 per cent of the total weight of the gluten. Under present processing conditions, one bushel of corn yields, on the average, about one pound of zein, although its actual zein content is two or three times this amount.

Zein differs from casein and soybean protein in that it is a prolamine and is soluble in aqueous alcohols. It appears to possess no free amino groups. It is manufactured commercially by counter-current extraction of fire-dried corn gluten with 85 per cent aqueous isopropyl alcohol at 55–60° during a period of 1.5 to 2.5 hours. The extract then contains 5 to 6 per cent zein and about 1 per cent xanthophyll oil. It is cooled to 15°, filtered to remove entrained and precipitated solids, and mixed with an equal volume of hexane, whereupon it separates into a two-phase solution which is centrifuged. Most of the hexane, together with most of the isopropyl alcohol, practically all of the xanthophyll oil, and a slight amount of protein separates as the lighter phase, while the heavy phase consists of 60 to 65 per cent isopropyl alcohol containing about 20 per cent zein. The latter mixture is then flashed to remove traces of hexane and the residual aqueous isopropyl alcohol solution of zein is pumped through nozzles into rapidly moving water, refrigerated to 50° F, at a 10 to 1 dilution ratio. The protein is thus coagulated and the isopropyl alcohol removed. The zein is then filtered, washed, and flash-dried.

Although 85 per cent isopropyl alcohol is utilized in this process, 92 per cent ethanol can also be employed. Methanol possesses insufficient

solvent power and promotes denaturation of the protein. Higher alcohols also possess poor solubility with respect to zein. Principal difficulties which must be overcome in this process are (1) a tendency toward denaturation (insolubilization) of zein solutions and (2) formation of a dough-like mass of wet zein at temperatures above 35 to 38°. Both of these troubles can be remedied by careful temperature control throughout the operations.

Although insoluble in water, zein is sensitive to it and is swelled thereby. It is stable to heat in the dry condition, but is easily denatured in the usual solvents upon heating or long standing. For each zein content, there is an optimum alcohol concentration for maximum stability. For example, 30 per cent zein solutions show maximum stability in ethanol of about 87–88 per cent by volume. Above and below this figure, stability is poorer. When rosin is added, stability increases with alcohol concentration. Denaturation is promoted by methanol regardless of its water content. Denaturation is autocatalytic. Zein dissolves in furfuryl- and tetrahydrofurfuryl-alcohols, in ethylene glycol and some of its derivatives, in mixtures of aromatic amines and alcohols, and in aqueous aliphatic alcohols and ketones. Certain organic acids and phenols are also solvents for zein.

Zein can be hardened, although slowly, with formaldehyde, especially under the influence of heat. Various materials inhibit cure, while others catalyze it. Ammonium salts, especially ammonium chloride, are the best catalysts. It is noteworthy that ammonium thiocyanate is particularly active, while the corresponding sodium salt is without effect. Other catalysts include acids and acidic salts of organic amines. From 2 to 8 per cent of formaldehyde will cure zein. Thin films may be heated two hours at 70°, or 15 minutes at 130° to bring about hardening. In general, the cured product exhibits higher tensile strength, better resistance to chemicals including water, greater flexibility, and higher softening point than the corresponding uncured material. Formaldehyde does not cure zein appreciably under neutral or alkaline conditions. Plasticized with such polar liquids as dibutyl tartrate or polyethylene glycols, zein can be converted into solid plastics, either with or without formaldehyde cure. The products vary in character from flexible films to rigid molded articles and rubber-like materials. All these substances possess water sensitivity which is attributable to both the protein and plasticizer. No thoroughly satisfactory plasticizer has yet been found for zein. Fatty acids containing 8 to 12 carbon atoms, dimerized fatty acids from soybean oil for example, fatty acid amides, mono esters of azelaic and sebacic acids, and diglycol phthalate have all been used to plasticize this protein.

The coating of paper to impart resistance to scuffing and grease, and to give gloss, decorative effects, and heat-sealing qualities, represents an important commercial use of zein which, for this purpose, may be applied either as a hot melt or in solution. A typical coating formula consists of 100 parts of zein, 80 parts of hydrogenated rosin, 40 parts of soybean fatty acids, 150 parts of denatured alcohol, and 25 parts of water. Coatings laid down from such a solution may, for example, be used to give protection against grease penetration to food wrappers. Zein has also been used to treat paper for other purposes. Pulp molded articles are made more rigid by dipping in an alcoholic solution of zein, with or without rosin. Paperboard, impregnated with an alcoholic zein solution and temporarily plasticized with lactic acid has been used in molding bottle caps and novelties. Zein-rosin mixtures have been added to paper stock in the beater to form a sheet having plastic molding properties.

An important application of zein is in the manufacture of shellac substitutes such as "Zinlac," "Kienle," "Melite," "Mantrose," and "Chem-lac." These products are stabilized solutions of zein and rosin or various resins in aqueous alcoholic media. A typical shellac substitute may contain equal amounts of zein and rosin, together with smaller amounts of various synthetic resins to increase shelf life.

Other developments are overprint coatings and adhesives containing zein.

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Chapter 25

Polymeric Organosilicon-Oxygen Compounds

History

Silicon and oxygen are the two most abundant elements in the earth's half-mile crust, being present to the extent of about 26 and 50 per cent, respectively. Silicon does not occur free in the elemental state. It was first isolated in amorphous form by Berzelius in 1823 and later as a crystalline allotrope by Saint Claire Deville in 1854. Silica and the inorganic silicates have been known and used since the dawn of time in a host of indispensable ways. Recent years have seen a gradual awakening of industrial interest in the organic esters of silicic acid. In 1944, the veil of wartime secrecy was lifted to announce the industrial availability of "silicones." The potentialities of these new organo-silicon oxide condensation polymers have been indicated by the wide variety of materials which have already been produced. Silicone products include liquids, compounds, resins, varnishes, lubricants, and elastomers, all characterized by a higher order of heat stability than conventional organic materials in the same physical form.

In 1863 the Frenchman, Wurtz, postulated a polymeric structure for silicic acid, comparing the repetition therein of the same structural group, joined through oxygen, with the similar situation which exists in polyglycols. Three years before then, Hofmann had suggested the use of ethyl silicate to prevent stone decay in Westminster Palace. Because chemical knowledge of this compound was then meager, Hofmann's idea proved impracticable at the time, but later studies have led to commercial application of hydrolyzed ethyl silicate as an impregnant for decreasing the porosity of stone, brick, and concrete, thereby improving resistance to spalling and crumbling on weathering.

More recently, ethyl silicate and its hydrolysis products have been recommended and used to some extent as a paint medium. This application, developed by King and Threlfall in England, attracted interest during the 'thirties. It was then found that hydrolyzed ethyl silicate improved the adhesion of various resin films to glass, especially enhancing resistance of the bond to water. Originally reported by Van Heuckeroth in conjunction with nitrocellulose, it was soon discovered that partic-

ularly interesting results were obtainable by incorporating partially hydrolyzed ethyl silicate with polyvinyl acetate or polyvinyl acetals such as the butyral. Observations of this kind at Mellon Institute led McGregor and Warrick to application of ethyl silicate in the formulation of adhesives for glass brick.

The advent of "Fiberglas" created a need for a heat resistant plastic or coating material for use in conjunction therewith in electrical insulation. "Fiberglas" and other inorganic insulating materials, including vitreous silica, quartz, mica, asbestos, ceramics, etc., are principally built on a framework of silicon and oxygen atoms. This need for a heat resistant varnish applicable to these substances was fulfilled by silicones as a natural outcome of research in glass at the Corning Glass Works and their search for a transparent plastic based on organo-silicon-oxygen compounds.

Studies in condensed organic silicates at Mellon Institute led to the discovery of other silicone products, both fluid and elastomeric, at Corning's Technical Glass Fellowship there. At the General Electric Company, interest in heat-stable, substantially inorganic insulation led independently to intensive development of silicones.

Silicones, a new class of insulating materials, resulted from fundamental research in the field of polymer chemistry bounded on the one hand by the organic plastics and on the other by the glasses and mineral silicates.

Commercialization of these interesting and novel products followed by the Dow Corning Corporation and the Resin and Insulation Department of the General Electric Company.

Organosilicon compounds were first studied in the laboratory by Friedel, Crafts, and Ladenburg between 1871 and 1874. Other investigators later worked in this field, but the major theoretical contributions were made by Kipping and his collaborators at the University of Nottingham in England. In 1904, Kipping discovered that Grignard reagents could be utilized in the preparation of organosilicon compounds. From then on, during the next three and a half decades, his school prepared and studied a large number of these substances, including many low polymeric condensation products. Kipping and his students tried to prepare the silicon analogs of the common organic derivatives, but they found the analogies few and the differences many—so many, in fact, that they laid the foundation for a large and growing field of chemistry.

The crux of modern silicone development is to be found in the basic work on the high polymer chemistry of silicones initiated during the last decade by J. F. Hyde and his associates at the Corning Glass Works and by R. R. McGregor and E. L. Warrick at Mellon Institute. E. G. Rochow

and his associates at the General Electric Company have also contemporaneously made important contributions to this field.

Chemistry

Although silicon can replace carbon in certain structures, the silicon-to-hydrogen bond is much less stable than that of carbon-to-hydrogen. Some silicon hydrides oxidize so readily that they take fire spontaneously at room temperature or slightly above. They also lose their hydrogen completely on treatment with aqueous solutions of alkalis. In both of these reactions, and in many others which silicon compounds undergo, the end-product is silicic acid which dehydrates to silica wherein extremely stable silicon-to-oxygen bonds are built up into a complex tridimensional polymer.

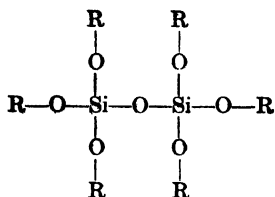
The silicon-to-silicon bond is also much less stable than that of carbon-to-carbon. Its instability increases with the number of silicon atoms which are joined to each other, so that silicon analogs of hydrocarbons containing more than six silicon atoms united to each other have not yet been isolated. The silicon-to-carbon bond, on the other hand, is an exceptionally stable one provided, at least, that the carbon atom is a member of a lower aliphatic or aromatic radical. Silicon tetramethyl, for example, is a liquid boiling at 26°. It is so stable that it can be purified by shaking with concentrated sulfuric acid. Although it burns readily and its flash point is below 15° F, yet it can be heated in the absence of oxygen to several hundred degrees Centigrade without decomposition. It is also reported that silicon tetraphenyl, a crystalline solid, can be sulfonated or chlorinated in the ring without affecting the Si—C bonds and can be distilled at red heat without decomposition.

In view of these facts, useful end-product organosilicon compounds thus far known contain silicon atoms attached only to carbon and oxygen. In order to create these bonds, however, it is usually necessary to pass through intermediates possessing the labile >Si-Cl group.

Silicon chlorides hydrolyze readily with water and undergo reaction with alcohols to form >Si-O-R . Ethyl orthosilicate, $\text{Si(OC}_2\text{H}_5)_4$, for example, is produced by reaction of silicon tetrachloride and absolute ethyl alcohol. Higher alkyl silicates can be obtained by ester interchange, as by reaction of ethyl silicate with tetradecanol.

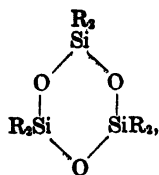
The alkyl esters of silicic acid can be readily hydrolyzed by reaction with water. For useful commercial applications of ethyl silicate predicated upon its ability to hydrolyze, alcoholic solutions of this ester are prepared and water is added in the amount theoretically required to

carry out the desired degree of hydrolysis. A catalyst is preferably added; hydrogen chloride is particularly effective, but many other chemicals are also applicable. Hydrolysis occurs with simultaneous polymerization, the average polymer size being controlled by the amount of water used and by the conditions. The dimer formed as the first product has the structure:



Higher polymers are obviously more complex. The final product of hydrolysis is silicic acid which dehydrates to silica.

The >Si-Cl bond reacts readily with water, forming the corresponding silanol, >Si-OH . Depending on the structure of the silicon chloride and the conditions of reaction, the silanol may be either a relatively stable product or an unstable intermediate which condenses at once to polymeric bodies. Where silicon tetrachloride is utilized, the product is silicic acid, the same material as that obtained by complete hydrolysis of ethyl orthosilicate. Where one or more chlorine atoms in silicon tetrachloride are replaced by alkyl or aryl groups, silanols or their condensation products are formed. Thus, where the silicon halide possesses only one chlorine atom per molecule, it yields an intermediate silanol, R_3SiOH , which undergoes dehydration to the corresponding disiloxane, $\text{R}_3\text{Si-O-SiR}_3$. Where the halide possesses two chlorine atoms per molecule, it hydrolyzes to an intermediate silanediol, $\text{R}_2\text{Si}(\text{OH})_2$, which is capable of condensing either to cyclic structures of which the simplest one is the six-membered ring compound,



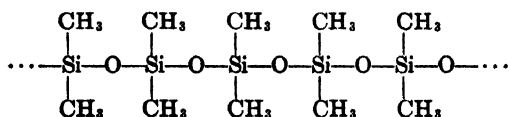
or to linear polysiloxanes, $(\text{-SiR}_2\text{O-})_n$, depending on conditions. Where the silicon halide possesses three chlorine atoms per molecule, it hydrolyzes to an intermediate silanetriol, $\text{RSi}(\text{OH})_3$, which is capable of tridimensional condensation to yield thermosetting plastics. The ease

with which a silanol condenses is in large part a function of the size and nature of the R group. The lower dialkyl silanediols, for example, condense so readily that they have not yet been isolated in the uncondensed state. Diphenylsilanediol, on the other hand, is a crystalline solid which can be isolated in high purity.

Hydrolysis products of silicon dichlorides were called silicones by Kipping because their empirical formula, R_2SiO , corresponds to that of the ketones, R_2CO . There is obviously no resemblance in structure between these two families and present practice tends to use the name silicone to cover generically all types of condensation polymers from the hydrolysis products of organosilicon chlorides. This name has, indeed, been applied even to the organosilicon chlorides themselves, but this use is regarded as an improper extension of its meaning by chemists active in this field. It should be emphasized that the term silicones applies only to those products which are derived from organosilicon chlorides in which at least one carbon-to-silicon linkage exists. Although condensed esters of silicic acid, previously described, are polysiloxanes, they behave very differently from the silicones from which they are differentiated structurally by the absence of direct carbon-to-silicon bonds.

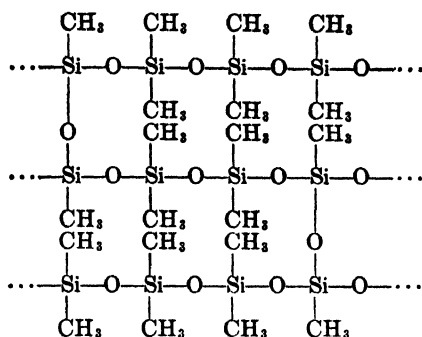
In commercial operations various silanols are produced by hydrolysis of methyl and phenyl silicon chlorides, especially. These intermediates, which may be partially condensed during their hydrolysis, are then further polymerized to linear or cross-linked products, depending on their nature and on the properties desired. Characteristics of the final products can be controlled by varying the radicals attached to the silicon atom, by admixing mono-, di-, tri-, and even tetrachlorides in suitable proportions, and by controlling conditions to yield condensation polymers of low, medium, or high molecular weight.

In the case of various fluid silicones and silicone rubbers, for example, the structure of a portion of the molecule may be represented as follows:

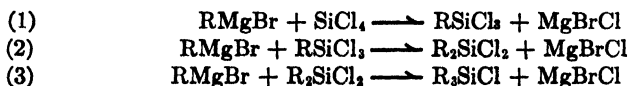


In certain products, ring structures similar to the six-membered silicone ring shown above may also enter complex polymeric molecules.

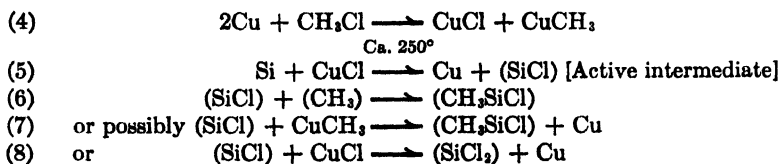
Cross-linking may be carried out, for example, by condensation of mono- and polyfunctional silanols. A typical portion of a cross-linked silicone may be represented as follows:



While several methods are known for the preparation of organosilicon chlorides, those used in commercial practice today are (a) reaction of a Grignard reagent with silicon tetrachloride:



and (b) catalytic reaction of elemental silicon with a hydrocarbon halide in the presence of metallic copper at temperatures of 250–300°. It has been hypothesized that the latter reaction may proceed through intermediate transitory formation of copper methyl as follows:



and so on until the silicon atom is tetra-substituted.

In the preparation of phenyl chlorosilanes by reaction of chlorobenzene with silicon, silver has been found to act as a catalyst and is apparently better than copper.

Properties

Hydrolyzed Ethyl Silicate. The final product obtained by hydrolysis of ethyl silicate, usually in aqueous alcoholic solution, is silicic acid which, on ignition, condenses to silica. It possesses the well-known refractory properties of this material, hence the use of ethyl silicate as means for depositing a siliceous bond in the production of refractory investments for casting alloy steels.

Where the hydrolysis is carried out in the presence of organic resins possessing free or latent hydroxyl groups, such as polyvinyl acetate or

the polyvinyl acetals, the resultant transparent film shows exceptional adhesion to glass, as well as other smooth surfaces, and the bond is unusually resistant to water immersion.

Silicones. Currently available silicones derived by condensation of hydrolytic products of organosilicon chlorides range from linear polymeric liquids boiling above 300° through rubber-like polymers to thermosetting plastics. All of these products are exceptional for their resistance to decomposition at elevated temperatures and their insensitivity to water and oxidizing agents.

Commercial grades of liquid silicones are water white, mobile fluids which possess low freezing points, low volatility at elevated temperatures, exceptional heat stability, and unusually low sensitivity to changes in temperature. The flow point may be as low as -85° in some cases, while they can be used continuously at 150° without oxidation or sludging. Typical characteristics of Dow Corning liquid silicones are listed in Table 181.

Viscosity-temperature relationships of several of the silicones listed in Table 181 are shown in Figure 315 and are there compared with typical hydraulic oils. These products are not only stable to heat, but they are also resistant to moisture, air and other oxidizing agents, and to many corrosive chemicals such as chlorine and gaseous hydrogen chloride. They are chemically inert and non-corrosive. They exhibit foam inhibiting characteristics where used in as little as 0.1 per cent concentration in conjunction with high temperature hydrocarbon lubricants in which they are insoluble. In carbon tetrachloride, toluene, and other organic liquids in which they are soluble, these silicone fluids promote foaming when shaken with air. They readily wet clean and dry glass, ceramic, and metal surfaces, rendering them water-repellent.

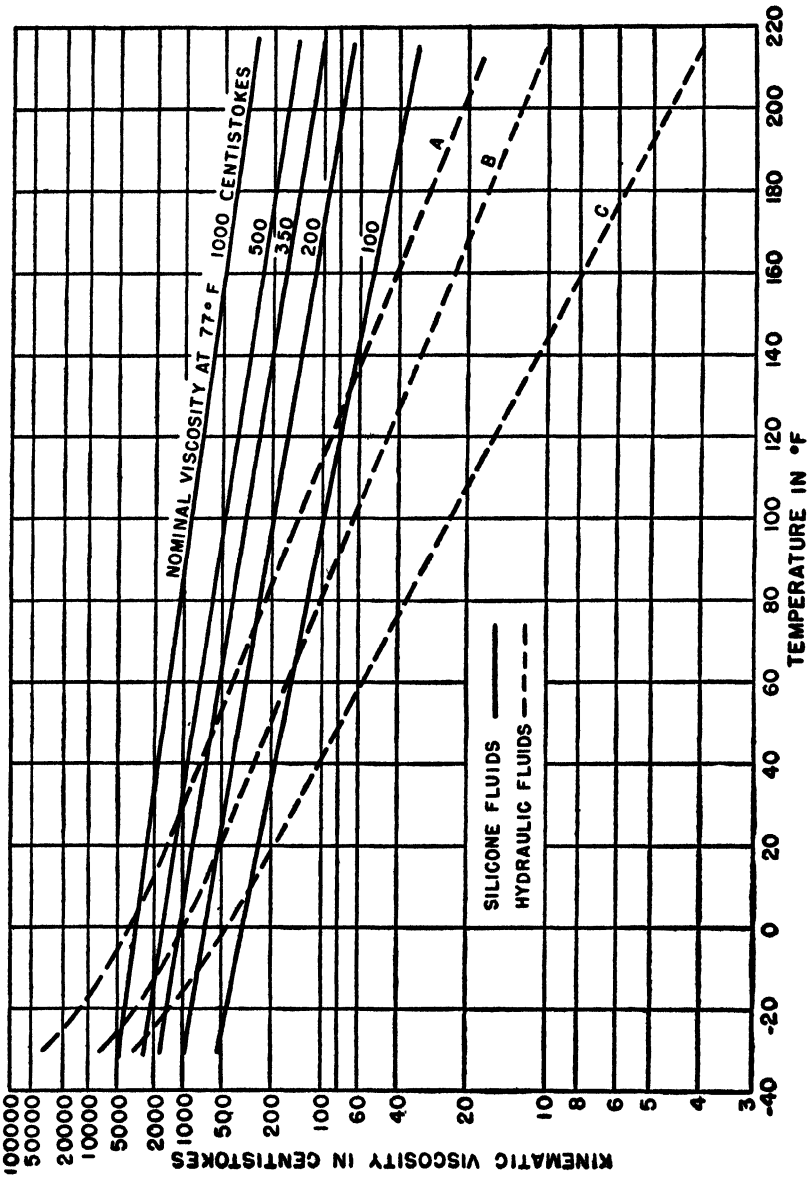
At 25° and 50 per cent relative humidity, non-volatile types of Dow Corning silicone fluids possess dielectric strengths of 250 to 300 volts per mil at 100 mils, volume resistivities in the order of 1×10^{14} ohm cms (not less than 10^{12} at 200°), and dielectric constants of 2.7 to 2.8 from 10^3 to 10^8 cycles per sec. Their power factors are less than 1×10^{-4} at 10^3 cycles per sec, 2×10^{-4} at 10^7 cycles per sec, and not more than 6×10^{-4} at 10^8 cycles per sec.

Silicone fluids are insoluble in water and the lower aliphatic alcohols, ethylene glycol, and lubricating oils. They are partially miscible with butyl alcohol, acetone, petroleum ether, and dioxane, and are miscible with aromatic hydrocarbons, chlorinated aliphatic hydrocarbon solvents, amyl alcohol, and many esters. They are incompatible with natural and synthetic rubbers and plastics and do not dissolve them even when hot.

Table 181. Physical Properties of Liquid Silicones ^a

Viscosity Grade in Centistokes 25°	Flash Point Minimum (°C)	Equilibrium Melting Point (°C)	(°F)	Specific Gravity 25°/25°	Refractive Index at 25°	Expansion Coefficient 10 ⁻⁶ per °C (25° to 100°)	Boiling Point Temp (°C)	Boiling Point Press (mm Hg)
0.65	-1	-68	-90	0.7606	1.3748	1.598	99	760
1.0	38	-86	-123	0.8182	1.3822	1.451	152	760
1.5	71	-76	-105	0.8516	1.3872	1.312	192	760
2.0	91	-84	-119	0.8710	1.3902	1.247	230	760
3.0	107	-70	-94	0.896	1.394	1.170	70-100	0.5
5.0	132	-70	-94	0.918	1.397	1.095	120-160	0.5
10.0	177	-67	-88	0.940	1.399	1.035	"	"
20.0	271	-60	-76	0.950	1.400	1.025	"	"
50.0	282	-55	-67	0.955	1.402	1.000	"	"
100.0	315	-55	-67	0.966	1.403	0.994	"	"
200.0	324	-40	-40	0.971	1.403	0.968	"	"
350.0	329	-40	-40	0.972	1.403	0.966	"	"
500.0	329	-40	-40	0.972	1.403	0.965	"	"
1000.0	338	-40	-40	0.973	1.4035	0.963	"	"

^a Non-volatile at 200° and 0.5 mm mercury.



Courtesy Dow Corning Corp. 13

Figure 315. Viscosity-temperature curves for Dow Corning Type 200 silicone fluids compared with typical hydraulic oils.

This property has led to their use as parting compounds in the molding of rubber and plastics.

Silicone elastomers retain their rubber-like characteristics throughout the range of -65°F to $+500^{\circ}\text{F}$, even on continuous use at these extreme temperatures. At 300°F , for example, certain compounded silicone elastomers will show only 10 per cent compression set after six hours of exposure to conditions which cause 100 per cent set of GR-S. They are not affected by ozone, corona, or ultraviolet light. The tensile strength of silicone rubbers so far available is low, although by suitable compounding it can be raised to 750 psi. Elongation ranges with the hardness of the compounded stock from 180 to 300 per cent.

Silicone resins exhibit good electrical characteristics combined with marked resistance to heat and moisture. Varnishes developed especially for electrical insulating applications are used in combination with such inorganic spacing materials as "Fiberglas," mica, and asbestos in HTS (high temperature silicone) insulation, conservatively rated as having a 50 to 75° advantage over conventional Class B insulation, such as high grade phenolic alkyd varnishes. With HTS insulation, continuous operation of electrical equipment at 175° is permissible and temperatures as high as 250° may be allowed for short periods. Dow Corning silicone resins and varnishes are supplied in 50 to 70 per cent concentration in various hydrocarbon solvents, particularly toluene and "Solvesso" No. 2. Dow Corning 993 varnish, especially designed to retain flexibility at high temperatures, is the silicone which has thus far been most widely used in HTS insulation. It must be cured by baking for 1 to 3 hours at 250° or for 6 to 15 hours at 225° . In thin sections, DC 993 has a dielectric strength of 1500 to 2000 volts per mil. Four-mil "Fiberglas" coated with DC 993 possesses a dielectric constant of 3.5 at 1000 cycles where tested at 25° and 50 per cent relative humidity. Its power factor is 0.7 per cent at 1000 cycles. HTS insulation does not track or carbonize on flashover.

For a detailed discussion of the electrical characteristics of silicone resins and of the spectacular service test results obtained with electrical equipment constructed with the use of HTS insulation, the references at the end of this chapter should be consulted.

Dow Corning silicone film is available in 1, 2, 3.5, and 5 mil thicknesses for use in durable high temperature insulation. It retains flexibility at 150 to 175° .

Applications

Hydrolyzed Ethyl Silicate. Ethyl silicate in hydrolyzed form, produced by addition of the requisite amount of water to an alcoholic solu-

tion of the ester containing a small amount of hydrochloric acid as catalyst, is utilized as a binder in making special foundry molds for investment casting of high melting alloys by the lost wax process. It can be used as a cement for many articles which have to withstand acids or high temperatures. It is an impregnating agent for porous articles such as silica brick, graphite molds, asbestos, concrete, and stone. It can be utilized as a component of certain paints and lacquers, especially as a vehicle for hard, heat-resistant coatings which are also resistant to chemical fumes. Application of hydrolyzed ethyl silicate in improving resin adhesion to glass has already been mentioned.

Silicones. Silicone fluids have been used as hydraulic and damping fluids, especially in precision instruments, as high dielectric fillers for electrical devices, as dashpot fluids, as foam inhibitors for high temperature lubricants—especially in the lubrication of Diesel engines, as heat-stable, inert, and high flash point liquids for oil baths, as impregnants for pump packings and gaskets, as low viscosity lubricants, as lubricants for application at both low and elevated temperatures beyond the range of most organic lubricants, and as lubricants or parting compounds in difficult molding jobs.

Dow Corning liquid silicones can also be used in water-repellent treatments for wood, plastics, glass, and ceramics. Waterproofing of radio coil forms and other insulators can be effected by dipping them in "Silaneal" (a 2 per cent solution of DC 200 fluid) and subsequently baking at an elevated temperature. Similar results have been obtained by the General Electric Company by exposure of hydrophilic surfaces at room temperature to methyl chlorosilanes in the vapor phase. Reaction occurs rapidly with deposition of a sub-microscopic film of silicone which renders the surfaces water-repellent. Paper, wood, cotton, and ceramic materials which have not been thoroughly dried or, preferably, which have been pre-conditioned at 50 to 90 per cent relative humidity may be made water-repellent either by exposing them to the vapor of methyl chlorosilanes or by dipping them in a liquid containing these silicone intermediates.

During World War II, a major portion of silicone production was devoted to Dow Corning No. 4 ignition sealing compound, used as a waterproofing and sealing agent in ignition systems of aircraft, tanks, and amphibious vehicles. This product has also found application in radar and other electrical devices. It is a smooth paste of such consistency that it can readily be applied by hand or by means of a grease gun. It is not only moisture-resistant itself, but it also imparts moisture-repellent characteristics to surfaces coated therewith. It possesses excellent resistance to arcing, while its temperature characteristics are similar to those described in the preceding section.

DC 7 compound is a translucent grease which does not melt. It is an oxidation-resistant lubricant, recommended for use over the temperature range of -70°F to $+400^{\circ}\text{F}$ in oxygen demand systems and in precision and control instruments. It can also be used as a lubricant in low pressure rubber bag molding.

Silicone greases have been introduced for high temperature lubrication and will operate for hundreds of hours at temperatures of $150-175^{\circ}$. Silicone compounds have been developed for use under severe service conditions as stop-cock greases and Nordstrom valve lubricants.

The exotic member of the silicone family, bouncing putty, should not go unmentioned.

Major applications for silicone rubber have been in tubing and cable subjected to high temperatures and in heat-resistant gasket materials. The General Electric Company developed the use of this material as a gasket for the edge of lenses of Navy searchlights and in the turbosuperchargers of B-29's. The Dow Corning Corporation produces silicone rubber (sold by them under the trade-mark "Silastic") as compounded, solvent-free salves ready for coating, molding, or extrusion. It is especially recommended for use in coating "Fiberglas" cloths for the fabrication of flexible, heat-resistant, water-repellent tape, molded diaphragms, gaskets, and flexible laminates. SC 75, which can be thinned with low-boiling mineral spirits, is also recommended for coating metal fabrics, wire wound resistors, and various metallic surfaces.

Silicone impregnating varnishes have found application in electrical insulation, especially in conjunction with "Fiberglas," asbestos, and mica. In this field they have provided manufacturers with constructional materials which permit design greatly improved over that practicable with standard Class B insulation. Thermal aging of insulation has previously imposed a serious limitation on the design of electrical equipment. Full advantage could not be taken of the inorganic spacing materials mentioned above because of the lack of high heat resistance on the part of the organic varnishes and impregnants used with them. HTS insulation affords unique heat-resistance, moistureproofness, and resistance to severe service conditions. It has allowed increased output, greatly prolonged life under adverse circumstances, decreased fire hazard, greater freedom from overload failures, and decrease in size and weight of electric motors.

Silicone magnet wire enamel is also available, as well as flexible, non-carbonizing film for use in condenser and coil insulation at temperatures of $150-170^{\circ}$.

Silicone coating resins have given an excellent account of themselves in protecting metal surfaces exposed to severe corrosion conditions and

high temperatures. Silicone bonded laminates of "Fiberglas" have been produced for electrical boards, slot wedges, and coil forms.

The surface of silicone applications has barely been scratched. Although this new family of polymeric substances has already gone far toward extending the temperature range of usefulness of a wide variety of engineering materials, still more spectacular developments and larger consumption of these products will undoubtedly occur during the next few years. Their current premium prices should decrease as the chemistry, technology, and applications of silicone chemistry expand.

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Chapter 26

Miscellaneous Resins

Innumerable resinous materials have been investigated from both theoretical and practical angles. Although the substances previously discussed in this text represent the most important plastics of commerce, many other synthetics of more or less resinous character have been developed and are now marketed for special purposes in relatively small volumes. Some of the most important ones will be mentioned in this chapter; many others cannot even be listed. A few plastics which have been studied extensively in industrial laboratories, but which still have not appeared on the market will also be considered. No attempt has been made to tabulate the thousands of other resinous materials which have not yet passed beyond the test-tube. Some of these infants of research and others now unborn will appear in commerce tomorrow.

Special low-melting glasses which, like "Mycalex," may contain powdered mica, as well as powdered metals which are molded by processes somewhat akin to those used by the plastics industry are chemically so unrelated to synthetic and semi-synthetic resins that they will not be discussed here.

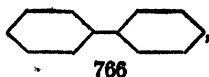
CHLORINATED PRODUCTS

In addition to the various chlorinated resins considered in preceding chapters, many others have been the subject of investigation. Among them, chlorinated biphenyl and chlorinated naphthalene are of importance. Chlorinated paraffin also finds use to a limited extent. These products are not truly resinous in the sense of being composed of extremely large molecules, but because of the complexity of their relatively small molecular units and because of the fact that they are often complicated mixtures, some of them approach the resinous state.

Condensation products of chlorinated toluene have provoked some interest, but are of little significance to date.

Resinous Derivatives of Biphenyl

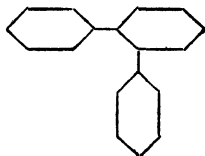
Biphenyl Production. Biphenyl,



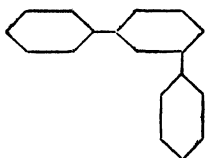
is manufactured industrially by pyrolysis of benzene. The latter hydrocarbon is preheated to 600–650° and cracked by bubbling through molten lead at temperatures in the order of 750–850°. Limited formation of carbon and hydrogen also occurs during this operation and may be decreased by replacing lead with molten mineral salts or salt mixtures, such as calcium and sodium chlorides which, in the ratio of 18:7, give a composition melting at about 600°.

More complicated ring systems are also formed as high-boiling by-products during this process and their ratio may be increased by elevation of the temperature or by use of less pure benzene, such as crude 90 per cent material.

By-products from Biphenyl—Terphenyl Waxes. From the high-boiling by-products it is possible to separate all three terphenyls, *ortho*:



meta:



and *para*:



These substances are isolated commercially, but despite their relative purity they possess certain wax-like characteristics. They are marketed under the trade-mark, "Santowax," being designated O, M, and P, respectively. Certain properties of these materials are listed in Table 182. In addition to these products, a mixture consisting largely of diphenyl and *ortho*-terphenyl is marketed under the designation, "Santowax" DO, the eutectic mixture of 71 per cent *o*-terphenyl and 29 per cent *m*-terphenyl is sold as "Santowax" OM, while other grades are designated as OSA and PSA. Hydrogenated *m*-terphenyl ("Santowax" MH) possesses a melting point of about 50° and hydrogenated *p*-terphenyl, a freezing point of 160°.

Table 182. Properties of the "Santowaxes" *

	"Santowax" Regular	"Santowax" M	"Santowax" O	"Santowax" P
Melting Point	140° primary hold point. 56° secondary hold point	83-85°	< 50°	209-213°
Flash Point	—	207°	171°	207°
Flame Point	—	—	193°	238°
Hardness (A.S.T.M. D-5-25)	—	0.23 mm	1.07 mm	0.33 mm
Density (25°)	1.10	—	—	—
Appearance	yellow waxy , solid	micro-crys- talline wax	oily, crys- talline	white, crys- talline
Boiling Range	80% between 365-402°	—	—	—

* Manufacturers' data. Monsanto Chemical Company.

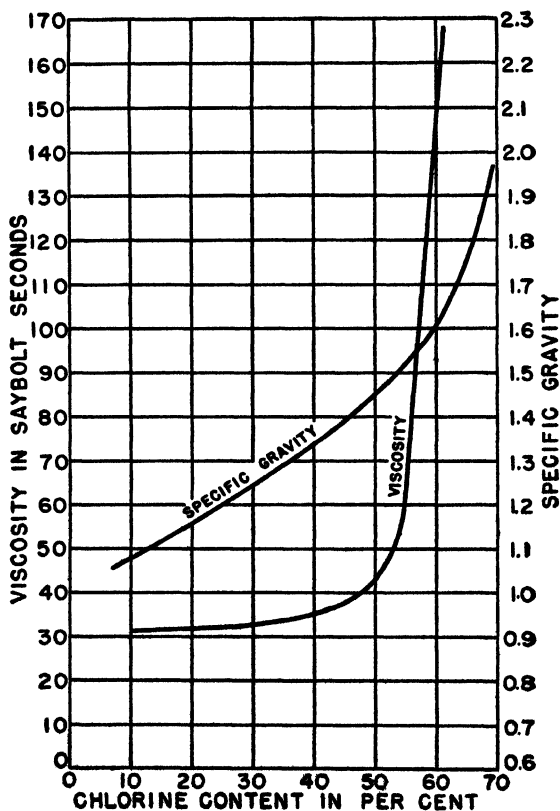


Figure 316. Relation between specific gravity, Saybolt viscosity at 210° F, and chlorine content of polychlorinated biphenyl. (Jenkins²⁸)

These materials are being developed as plasticizing compounds in the formulation of paints and inks, as plasticizers and opacifiers for various waxes, as agents for use in waxing citrus fruit, and as components of diverse polishes, cosmetics, and paper coatings.

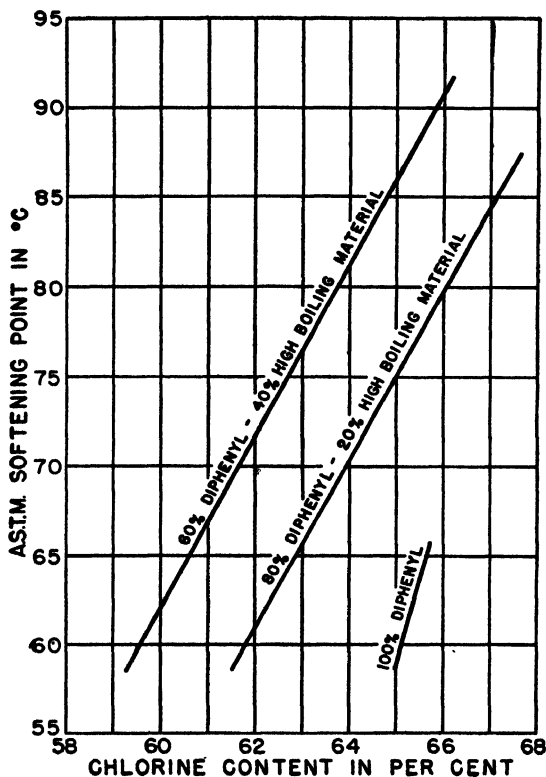


Figure 317. Ring and ball softening point (ASTM D36-24) of chlorinated biphenyl as influenced by chlorine content and by admixture therewith, prior to chlorination, of varying amounts of high boiling material (b.p. 270–400°) obtained as a by-product during pyrolytic conversion of benzene to biphenyl. (*Jenkins*²³)

Chlorination Products of Biphenyl. Chlorination of biphenyl at elevated temperatures in the presence of such catalysts as iron yields a series of mixed chlorinated derivatives ranging from viscous liquids to high-melting, brittle, more or less resinous solids. At 60–80°, the principal product is a liquid mixture of 2- and 4-monochlorobiphenyls, provided reaction is stopped when only 80–95 per cent of the theoretical amount of chlorine for monochlorination has been absorbed. Further chlorination with increase of temperature up to 175–220° permits introduction of as

Table 183. General Physical Prop-

Form	Aroclor 1242 Practically colorless mobile oil	Aroclor 1248 Yellow tinted oily liquid	Aroclor 1254 Yellow tinted viscous oil	Aroclor 1260 Light yellow soft, sticky resin
Color—NPA	0.5 max	0.5 max	1.0 max	1.0 max
Acidity—maximum (mg KOH per g)	0.01	0.01	0.01	0.015
Coefficient of expansion cc/cc/° C	0.000678 (25–65°)	0.000702 (25–65°)	0.000661 (25–65°)	—
cc/cc/° F	0.000377 (77–149° F)	0.000389 (77–149° F)	0.000367 (77–149° F)	—
Density—specific gravity 25°/25° (77°/77° F)	1.378 to 1.388	1.447 to 1.457	1.538 to 1.548	1.618 to 1.629
Pounds per gal.—25° (77° F)	11.50	12.08	12.83	13.50
Distillation range—A.S.T.M. D-20 Mod. ° C	322–365 Uncorr. 612–689 Uncorr.	330–370 Uncorr. 626–698 Uncorr.	365–390 689–734	385–420 725–788
° F				
Evaporation Loss—%—A.S.T.M. D-6 Mod: 163° 5 hr	3.04 to 3.64	3.0 to 4.0	1.06 to 1.28	—
100° 6 hr	—	—	0.4	0.0 to 0.2
Flash Point—Cleveland Open Cup: ° C	176–180	193–196	None	None
° F	348–356	379–384		
Fire Point—Cleveland Open Cup: ° C	334	None	None	None
° F	633			
Pour Point—A.S.T.M.: ° C	–17.7 to –20.7	–7	8 to 12	26 to 36
° F	–0.2 to –5.3	19.4	46 to 54	79 to 97
Softening Point—A.S.T.M.: ° C	—	—	—	—
° F	—	—	—	—
Refractive Index—D-line—20°	1.627–1.629	1.630–1.631	1.637–1.639 at 25° C	—
Viscosity—Saybolt Universal Sec (A.S.T.M.—D-88)				
210° F (98.9° C)	34.0–34.6	36.0–37.0	43.5–48.5	70–82
130° F (54.4° C)	49–56	69–78	260–400	2600–4500
100° F (37.8° C)	80–93	185–240	1800–3800	—

many as 7–8 chlorine atoms per molecule of biphenyl. The relation between density, viscosity, and chlorine content of chlorinated biphenyl is shown in Figure 316.

Chlorination of mixtures of biphenyl and the high boiling by-products of biphenyl manufacture yields resinous materials possessing higher melting points than pure biphenyl chlorinated to the same degree, as illustrated in Figure 317.

Color of these products can be improved by vacuum distillation or by carrying out chlorination in the presence of iodine as a catalyst.

Chlorinated biphenyl, manufactured by the Monsanto Chemical Company under the trade-mark "Aroclor," is available in chlorine contents ranging from 18 to 66 per cent and in physical forms varying from liquids to resinous solids and refractive amorphous flakes. The more highly chlorinated products do not support combustion. In general, they are characterized by high dielectric constant, resistivity, and dielectric strength, and by low power factor. Their electrical properties have

Properties of Some of the Aroclors*

Aroclor 1262	Aroclor 1268	Aroclor 1270	Aroclor 4465	Aroclor 5442	Aroclor 5460	Aroclor 2565
Light yellow sticky clear resin	Pale yellow opaque brittle resin	White crystalline powder	Yellow transparent brittle resin	Yellow transparent sticky resin	Yellow transparent resin	Brown-black opaque resin
1.2 max 0.02	—	— 0.175	1.5 max 0.05	— 0.028	2.0 max 0.07	— 1.26
0.000640 (25–90°)	—	—	0.000611 (25–65°)	0.00123 (25–99°)	0.00179 (25–124°)	0.000856 (25–65°)
0.000355 (77–194° F)	—	—	0.000339 (77–149° F)	0.000683 (77–210° F)	0.000994 (77–255° F)	0.000364 (77–149° F)
1.646 to 1.653 13.72	1.804 to 1.811 15.13	1.944 to 1.960 16.24	1.712 to 1.723 14.28	1.432 to 1.447 11.96	1.740 to 1.745 14.50	1.724 to 1.740 14.41
373–404 Uncorr. 703–759 Uncorr.	—	450–460 842–860	Requires vacuum Requires vacuum	—	Requires vacuum Requires vacuum	—
0.48 to 0.56 —	0.15 to 0.24 —	0.0 to 0.1 —	0.23 to 0.29 —	2.0 0.012	0.025 1.51 to 1.71*	0.21 to 0.24 —
None	None	None	None	247° 477° F	None	None
None	None	None	None	> 350° > 662° F	None	None
34.9 to 38.0 95 to 100.4	—	—	—	46 115	—	—
—	135 to 160 †	294 to 300 †	60–66	48.5 to 53	100 to 105.5	70 to 77
—	275 to 320 †	561 to 572 †	140 to 151	119 to 127	212 to 222	158 to 171
1.6501–1.6517	—	—	1.664–1.667	—	1.660–1.665	—
90–103 600–850 at 160° F	—	—	92–156 ‡	313.5	—	—

* At 260° — 5 hr

† Hold pt.

‡ 266° F or 130° C

been reported in some detail by Clark⁵ and by White and Morgan.⁵¹

Chlorinated biphenyls are exceptionally stable towards both acids and alkalis, being unaffected by boiling solutions of sodium hydroxide. They dissolve in practically all organic solvents except those which contain water or which, like glycerol, possess several hydroxyl groups in the molecules. They are incompatible with cellulose acetate and manila gum, but compatible with most other natural and synthetic resins. Resinous chlorinated biphenyls adhere well to smooth surfaces such as glass and metals. They do not corrode the latter. Although relatively non-toxic, prolonged exposure to vapors of these materials, oral ingestion, or repeated external contact should be avoided.

The resinous "Aroclors" are thermoplastic friable solids which show more or less cold flow, depending upon softening point. They are unsuitable for use as a binder in molding compositions, but find application in combination with other resins in the formulation of surface coatings and adhesives. They are also utilized in waterproofing paper and decorat-

ing glass. Other uses include high temperature lubricants and fluids for transmitting hydraulic power. An important application is to be found in their use as a component of insulating compositions, especially non-flammable transformer oils. General physical properties of these materials are listed in Table 183.

Chlorinated Naphthalene

Naphthalene, like biphenyl, may be exhaustively chlorinated to yield complex liquid or solid mixtures of polychloro substitution products. Inasmuch as commercial materials of this kind are stable to hydrolysis and

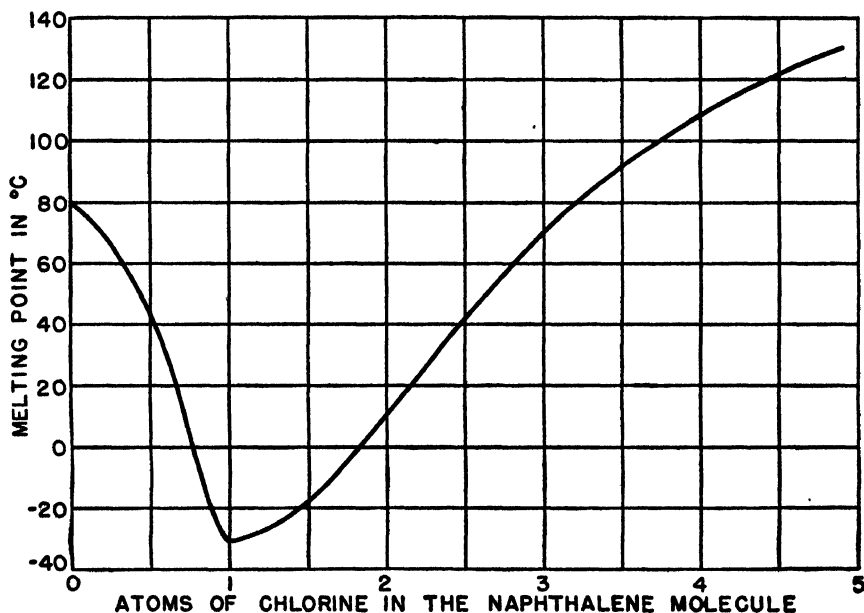


Figure 318. Melting point *vs* composition of chlorinated naphthalene. (Engelhardt¹⁸)

do not corrode copper, except under high temperatures or in the presence of moisture, it is probable that they contain only minor amounts of ring addition products.

Chlorination may be carried out in either the liquid or vapor phase, as well as in solution, customary carriers such as chlorides of iron, aluminum, or antimony being effective catalysts.

Polychlorinated naphthalenes, like polychlorinated biphenyls, are not truly resinous for it is possible to separate crystalline compounds from them. Solid products are wax-like and may contain as much as sixty per cent chlorine. They vary in color from black to light green-yellow

and are produced in flow points ranging from 65 to 130°. The relation between softening point and chlorine content is indicated in Figure 318.

Polychlorinated naphthalenes are sufficiently low in molecular weight to boil at temperatures ranging from 290 to 370°. Their specific gravity varies between 1.5 and 1.7 at room temperature. They possess high dielectric strength and excellent specific inductive capacity (4.5 to 5.5). They are non-corrosive and insoluble in and substantially unaffected by alkaline and acid solutions. They are extremely water-resistant, non-flammable, and soluble in practically all organic oils and solvents.

Sold under the trade-mark, "Hallowax," the electrical and non-flammable characteristics of polychlorinated naphthalenes adapt them to a variety of insulating applications, including components of wire coatings, impregnants for textile wire coverings, sealants for relay and transformer coils, and impregnants for paper wound condensers. They also find use as high melting waxes in polishes, surface coatings, and plasticizing compositions.

Polychlorinated naphthalenes are also available from Hooker Electrochemical Company in melting point grades of 93° and 135°.

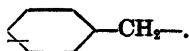
Chlorinated Paraffin

Paraffinic petroleum cuts can be chlorinated readily to yield products containing from one to several chlorine atoms per molecule. Although chlorination of the lower paraffins is best carried out under carefully controlled conditions of light, heat, and catalytic influence, the substitution of chlorine for the hydrogen of higher aliphatic hydrocarbons proceeds readily without being critically affected by any of these agents. Partially chlorinated paraffins are now vitally important chemical intermediates used in the manufacture of such industrial products as synthetic detergents and pour point depressants for lubricating oils. More highly chlorinated paraffins are made by the Hooker Electrochemical Company and by Hercules Powder Company and are recommended as plasticizers and flameproofing agents. It is said that resistance to water, weather, and mildew is also thereby imparted to fabrics. Hercules' products containing 42 and 70 per cent chlorine are marketed under the trade names "Clorafin" 42 and "Clorafin" 70, respectively. Like most of the chlorinated paraffins commercially available, "Clorafin" 42 is a pale, viscous liquid. "Clorafin" 70 is likewise pale-colored, but is hard, resinous in appearance and possesses a ring and ball softening point of 90–100° C. Densities of "Clorafin" 42 and "Clorafin" 70 fall within the ranges of 1.162–1.175 and 1.60–1.65, respectively. Analogous products possessing the same chlorine contents and being a viscous liquid and powdered resin, respectively, are available from Hooker under the design-

nations, "CP-20" and "CP-70." A chlorinated propane, possessing the average formula $C_3H_{0.15}Cl_{7.85}$, is also available from Hooker in experimental quantities under the designation "Chloropropane Wax 130." It is a tough, white crystalline wax of melting point range: 110–155°, and boiling point range: 210–270°. It is insoluble in water, but soluble in alcohol, ether, and most chlorinated solvents.

Benzyl Chloride Resins

There has been some industrial effort to develop soluble varnish resins from benzyl chloride produced by the action of chlorine on toluene in the presence of light and absence of ring halogenation carriers such as iron. Aluminum chloride and other Friedel-Crafts catalysts are effective in bringing about self-condensation of benzyl chloride with elimination of hydrogen chloride and formation of a dark-colored polymeric material composed largely of the group,

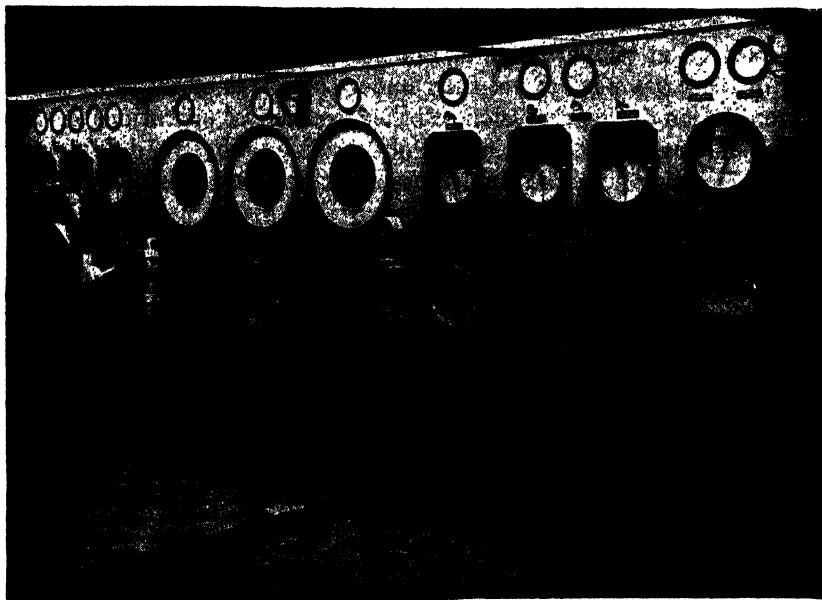


Most of the chlorine is eliminated during condensation, so that the resin is primarily hydrocarbon in nature, but end chlorine groups may still be present. Molecular weight can be decreased and solubility increased by modification of these resins with aromatic hydrocarbons or phenols during condensation. Commercialization of benzyl chloride resins is almost non-existent today.

FLUORINATED POLYMERS

A halogenated polymer which is entirely different in character from others discussed in this text is to be found in polymerized tetrafluoroethylene, $(CF_2=CF_2)_n$. This product was manufactured for highly secretive wartime applications during World War II, pilot plant production of commercial quantities having been commenced by du Pont in 1943. The trade-mark "Teflon" has been adopted by du Pont for this polymer which is regarded as a truly outstanding product.

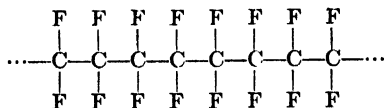
"Teflon" is of exceptional interest on both technical and practical grounds. It has often been assumed that carbon-to-carbon unsaturated systems bearing no hydrogen atoms do not polymerize. This supposition is strikingly disproved by polytetrafluoroethylene which contains no hydrogen. Much as the study of silicones has opened a new field of high polymers endowed with special characteristics imparted by the carbon-to-silicon grouping, so the evolution of polytetrafluoroethylene bids fair to initiate development of a whole new category of resinous materials possessing unique properties attributable to organically combined fluorine.



Courtesy E. I. du Pont de Nemours & Co.

Figure 319. Control panel used in manufacturing "Teflon." Controlled at this one panel is all the equipment for refining the monomer and producing the polymer from which is made du Pont's unique industrial plastic "Teflon" tetrafluoroethylene resin. Able to withstand high temperatures and the most corrosive acids better than any other plastic, "Teflon" is also an excellent insulator for high-frequency currents.

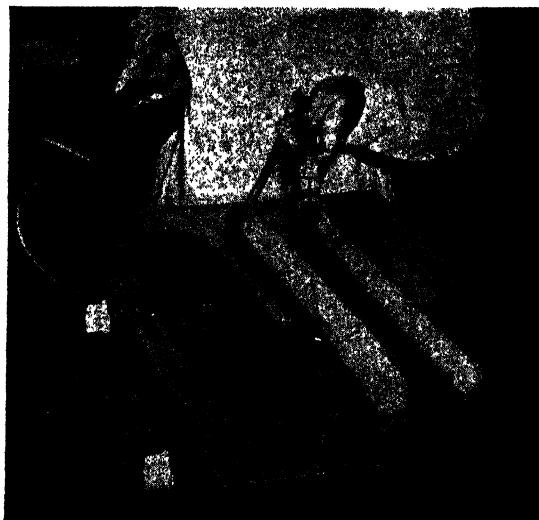
Monomeric tetrafluoroethylene is gaseous under normal conditions. By application of pressure, even at room temperature or below, it can be converted to a solid, tough, granular polymer possessing a linear structure of which a portion may be represented as follows:



According to United States patent No. 2,230,654, silver nitrate, especially in the presence of methanol, exercises a catalytic influence on this polymerization.

"Teflon" is transparent in thin sections, but white to gray in thicker ones. Although tough, it possesses a wax-like feel and appearance. It is remarkably resistant to heat and can be used throughout the temperature range of -150° to $+575^{\circ}$ F. Polytetrafluoroethylene becomes incandescent when held in a flame, but does not burn upon removal therefrom.

Extremely small amounts of fluorine-containing gases, however, are said to be given off at temperatures as low as 400° F. Inasmuch as the toxicology of these gases is not yet fully understood, it is essential to provide good ventilation during extrusion or other mechanical operations in which this temperature may be attained. Polytetrafluoroethylene does not possess a true melting point, but undergoes a solid phase-transition at 620° F



Courtesy E. I. du Pont de Nemours & Co.

Figure 320. Plastics on the grill. "Teflon" tetrafluoroethylene resin, du Pont's new industrial plastic, retains strength and form at higher temperatures than any known organic material. Temperature of the hot plate shown above is about 390° F. Rods of two other plastics have melted or swelled out of shape. "Teflon" is unaffected. Gaskets and wire insulation for jet engines are made of this plastic, which is unharmed by temperatures ranging up to 575° F.

with a sharp drop in strength. At about 750° F it slowly decomposes to yield gaseous products.

The electrical characteristics of "Teflon" are also exceptional, especially when considered in conjunction with its heat-resistance. It possesses excellent resistance to surface arc-over. On failure it does not carbonize, but vaporizes without deposition of a conducting path. Electrical losses are comparable to those of polyethylene and polystyrene and are substantially constant over the frequency range of 60 cycles to 3000 megacycles.

Chemical resistance of "Teflon" is likewise outstanding. It withstands attack by all materials except molten alkali metals and can be boiled in

aqua regia, hydrofluoric acid, and fuming nitric acid without change in either weight or properties.

Characteristic physical properties of "Teflon" are given in Table 184.

Table 184. Typical Properties of "Teflon"*

(Data given represent standard commercial grades of material and standard methods of testing except where otherwise noted)

Property	Test Result	Test Method
Specific gravity	2.1-2.3	D792-44T
Tensile strength at 77° F, psi	2000-4500	D412-41T ⁽¹⁾
Elongation at 77° F, %	300-400	Die C ⁽¹⁾
Flexural strength at 77° F, psi	2000	D650-42T ⁽²⁾
Stiffness at 77° F, psi (0.125 inch)	60,000	D747-43T
Impact strength, Izod, — 70, 77, 170° F, ft-lb/inch	2.0, 4.0, 6.0	D256-41T
Hardness, durometer D	55	—
Compressive strength, psi at 0.1 % deformation	1700	D695-42T
Yield temperature, ° F	> 320	Arl. M-8
Heat distortion temperature, low load, ° F	266	D648(b)-44T
Specific heat, cal/g/° C	0.25	— ⁽³⁾
Coefficient of expansion per ° F (77-140)	5.5×10^{-5}	D696-42T
Thermal conductivity BTU/hr/sq ft/° F/in (0.18 inch)	1.7	Arl. P-32 ⁽⁴⁾
Brittleness temperature, ° F	< - 150	D746-43T
Dielectric strength, short time, volt/mil (0.080 inch)	480	D149-40T ⁽⁴⁾
Volume resistivity, ohm-cm	10 ¹⁸	D257-38
Dielectric constant 60, 10 ³ , 10 ⁶ , 10 ⁸ , 10 ¹⁰ cycles	2.0	D150-40T
Power factor 60, 10 ³ , 10 ⁶ , 10 ⁸ , 10 ¹⁰ cycles	<0.0002	D150-40T
Water-absorption, %	0.00	D570-42 ⁽⁶⁾
Moisture permeability g/sq m/24 hr	0.00-0.5	D697-42T
Outdoor weathering	No detectable change in 1 year	

⁽¹⁾ Tensile strength in oriented film may be as high as 15,000 psi

⁽²⁾ Specimens do not break

⁽³⁾ Method of mixtures

⁽⁴⁾ Cenco-Fitch apparatus

⁽⁵⁾ 1000-2000 volt/mil in 5 to 12-mil thickness

⁽⁶⁾ Not wet by water

* Manufacturers' data. E. I. du Pont de Nemours & Co., Inc.

"Teflon" can be machined easily with standard wood- and metal-working tools. Sheet stock can be handled on a punch press. Thin-walled tubing can be flared by methods applicable to copper tubing, while heavy tubing can be threaded with a standard pipe threader.

This plastic is available in the form of rods, tubes, sheets, beading, gaskets, and thin tapes. Production of special molded shapes by du Pont will be considered where feasible. Molding powders are not currently available because of the difficulty of fabrication technique. Complicated shapes can be produced at present only by machining one of the standard available forms just listed. Sheets and thin films are made by shaving baked blocks and cylinders. Rods and tubes are extruded in continuous lengths by screw stuffers using special techniques. Extrusion rates are

slow. Wire can be coated, although slowly, by using a crosshead die on a screw stuffer with careful control of rates and temperatures.

"Teflon" is suggested for use in containers for holding preforms in electronic heaters, in molds of certain types, as gasketing and packing material and as tubing for chemical process work. It is also recommended as a dielectric in coaxial cable for color television and radar.

Modifications of "Teflon" adaptable to injection and compression molding are under development. These products will also possess good electrical properties as well as resistance to chemicals and heat.

POLYGLYCOLS

In 1863, the French chemists Wurtz and Laureço prepared polyethylene glycols, recording their results in the *Annales de chimie et de physique*. The former worker obtained these products by heating ethylene oxide with water whereby he obtained not only glycol itself but also polymeric bodies. The latter chemist heated ethylene glycol with ethylene dibromide and obtained similar materials. It is significant that the polymeric nature of these substances was recognized at that early date, and formulas ranging up to $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_6-\text{H}$ were assigned to various impure cuts separated by fractional distillation. It is also of interest that, on the basis of the Theory of Types then prevalent, Wurtz in 1863 compared the probable formulas of polyethylene glycol, silicic acid, and stannic acid, and pointed out structural similarities between these organic and inorganic substances—that is to say, repetition of the same group many times, joined through oxygen bridges. Wurtz' ideas have been confirmed in recent years by the researches of Willstätter, Staudinger, and others.

Ethylene oxide can be polymerized readily to high molecular weight products by contact with numerous basic catalysts such as sodium or potassium hydroxide, sodamide, tertiary amines like trimethyl amine, and alkali metals. Acidic catalysts are effective in some cases. Stannic chloride, for example, causes polymerization even at -80° . It is also possible to carry out polymerization of ethylene oxide by passage of the gas over suitable catalysts above 100° . Alkaline catalysts are likewise preferred here, but acidic materials may be used. The products range in degree of polymerization from 3 to about 300, with corresponding molecular weights running from 160 to 13,000. By use of such moderate catalysts as oxides of strontium, calcium, and zinc, or their carbonates, Staudinger has prepared eucolloids possessing molecular weights up to about 120,000. These products range in character from viscous liquids, through semisolid salves, to wax-like solids. Eucolloidal polymers are more fibrous solids. The general formula assigned to polymers of

ethylene oxide is that of polyglycols, *i.e.*, polyethers in which the end groups are hydrated to hydroxyls:



Table 185 shows the relationship found by Staudinger between molecular weight and softening point of the polyglycols.

Table 185. Influence of Molecular Weight upon Melting Point, Viscosity, and Solubility of Polyglycols ^{44, 46}

Molecular Weight	Degree of Polymerization	Approximate Melting Point	Relative Viscosity in Water	Relative Viscosity in Benzene	Solubility in Ether
(1 molar solution)					
430 } 440 }	10	Liquid	—	—	Soluble in cold ether
1,230 } 1,350 }			30	35°	
1,550 } 1,720 }	35	50°			1.3425
3,200 } 3,280 }			75	56°	
4,650 } 4,900 }	110	59°			1.6312
13,000 }			300	70°	
100,000 }	2500	175°	—	—	—
(with decomposition)					

(with decomposition)

Polyglycols derived from olefins higher than ethylene can be obtained by similar processes.

Polyethylene glycols are marketed in this country, under the trade name "Carbowax" by the Carbide and Carbon Chemicals Corporation. They are soluble in both water and aromatic hydrocarbons. Because of their unique solubility characteristics, the "Carbowax" compounds are indicated as agents for assisting mutual solubility of these immiscible liquids. They are recommended as water-soluble lubricants in metal-forming operations and for textile fibers and rubber molds. They are used as plasticizers and softeners in glues and composition cork. They are also utilized as components of printing inks, water-soluble paints, paper coatings, kalsomines, sizes, cosmetic creams and lotions, hair dressings, including permanent wave conditioners, pharmaceutical preparations such as iodine carriers, and numerous other applications.

Esters and ethers of polyethylene glycols derived from higher fatty acids and alcohols are valuable non-ionic surface active agents. The former are available under such trade names as "Emulphor" and "Neutronyx."

Characteristic properties of "Carbowax" 1500 and 4000 are listed in Table 186.

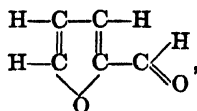
Table 186. Properties of Certain "Carbowaxes" ⁴

			"Carbowax" 1500	"Carbowax" 4000		
Density (g/cc at 20°)			1.152	1.203		
Melting Point (° C)			35-37	50-53		
Viscosity (Saybolt Universal seconds at 210° F)			78	418		
Flash Point (° F)			430	535		
Solubility (g/100 cc)		20°	50°	20°	50°	
	{	Water	> 100	complete	> 100	> 100
		Acetone	> 100	complete	> 100	> 100
		"Cellosolve"	> 100	complete	40	> 100
		Ethanol	> 100	complete	33	> 100
		Ethyl acetate	> 100	complete	43	> 100
		Heptane	< ca. 0.01	ca. 0.01	< ca. 0.01	< ca. 0.01
		Toluene	> 100	complete	43	> 100

Figure 321 shows the relation between freezing point range and average molecular weight of commercial products, while Figure 322 is a phase diagram for aqueous solutions of "Carbowax" 4000.

FURANE RESINS

Furfural,



first made by Dobereiner in 1830 while preparing formic acid by reaction between sulfuric acid, manganese dioxide, and sugar, is now manufactured on a large scale from agricultural wastes, particularly oat and cottonseed hulls. The Quaker Oats Company commercialized this chemical in 1922, using by-product hulls from rolled oats. The pentosans of the raw materials are hydrolyzed to pentoses and dehydrated to the aldehyde by subjecting seed hulls to the action of steam and dilute sulfuric acid while the mass is agitated in digesters. Furfural is separated from the distillate by fractionation.

Uses for furfural developed slowly over a period of years, a single American plant producing sufficient quantities of this chemical to satisfy the limited demand for many years. Since the development of the synthetic rubber program, furfural has been found to be an excellent selective solvent for purification of butadiene. It has therefore lately been much in demand and a plant has been erected to fill this increased need, using cottonseed hulls as raw material.

Furfural and its derivatives can serve as the basis for several different types of resins. The presence of unsaturation, of conjugation of unsaturation, including conjugation of the carbonyl group, of a relatively labile five-membered heterocyclic ring, of pseudo-aromatic properties

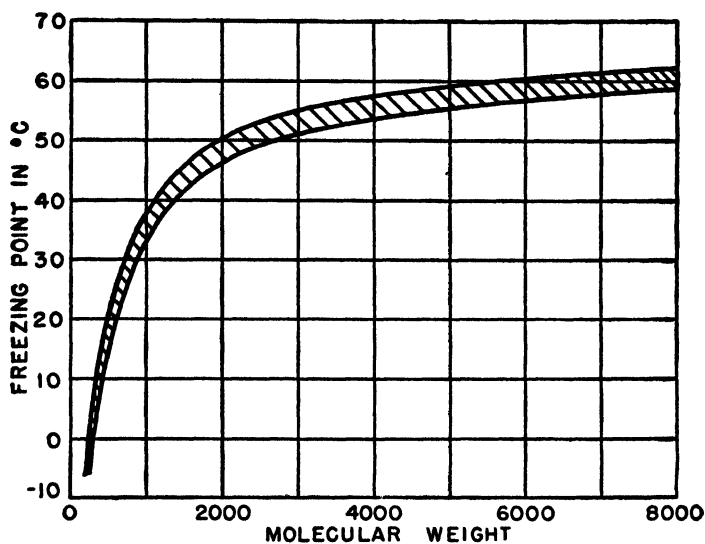


Figure 321. Freezing-point range of polyethylene glycols as a function of molecular weight. (McClelland and Bateman²⁵)

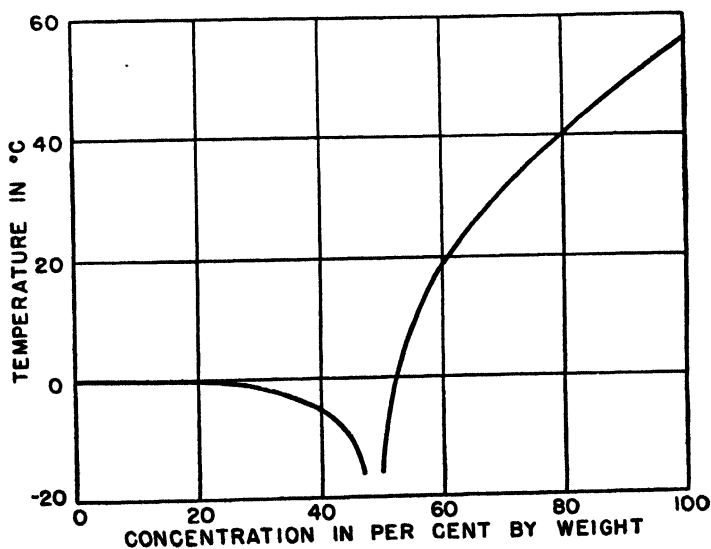


Figure 322. Phase diagram of aqueous solutions of polyethylene glycol of 4000 M. W. ("Carbowax 4000"). (McClelland and Bateman²⁵)

conferred by this ring, and of an aldehyde group, all lend numerous resin-forming potentialities to this compound. In addition to the resinophores present in furfural itself, it can also be converted to numerous chemical derivatives, many of which are capable of resinification.

Phenol-Furfural Resins

The earliest commercial application of furfural in the domain of plastics was in substitution for formaldehyde in the production of phenolic resins. Even here, although these resins have been known for two score years, only lately have they become well-developed under the trade name, "Durite." Phenol-furfural resins have been discussed in greater detail in Chapter 6.

Furfural-Lignin Plastics

A more recent use of furfural in the resin field has been in the production of lignin plastics, especially those derived from bagasse and redwood wastes. These furfural-converted products are still in the process of development. They have been mentioned in Chapter 23 under Lignin Plastics. In addition to the use of furfural in activating the lignin components of these waste materials, other resins derived from furfuryl alcohol and formaldehyde, mentioned in the next section, have found utility in combination with lignin and, especially, in admixture with activated redwood wastes.

Furfuryl Alcohol-Formaldehyde Resins

Furfuryl alcohol can be reacted with formaldehyde to yield a viscous mass which can be cured to a thermoset composition by application of heat. An acid catalyst is normally used, such as hydrochloric, phosphoric, or benzoic acid. The reaction can also be catalyzed by alkaline materials to yield resins which are much more thermoplastic than acid catalyzed types. Resins of this general character have been developed by the Irvington Varnish and Insulator Company and are marketed in particular under the designation "Irvington" 1226 resin. Containing no phenol, this resin behaves in much the same manner as phenolics, yielding thermoset products after curing. "Irvington" 1226 resin can be used as a binder with numerous fillers. In admixture with activated redwood wastes, especially, it has been utilized in several plastics. One of them, manufactured by the Vulcanized Rubber and Plastics Company under the name "Colemorite," has found application principally as a replacement for hard rubber in such articles as fan blades. Properties of "Colemorite" and of certain other similar products have been given on page 733.

Using "Irvington" 1226 resin, the Lehon Company, during the war, attempted to develop a compression-molded jettison gasoline tank for the Army Air Corps at Wright Field. Development of this tank was originally begun at a time when threatened shortages of metals made it necessary to find a satisfactory substitute for steel and aluminum. The tank was an external knockdown type designed for installation on the P-47, P-51, and P-39 fighter planes for which the increased range afforded by jettison tanks was desired. Its capacity was 75 gallons. It was made from rag stock, redwood powder, and this furane resin, the molding compound being prepared by Banbury mixing. It was cured under high pressure in a single-cavity mold on extremely large presses of the American Hard Rubber Company. The temperature was held at 325–350° F for about 15 minutes, breathing being allowed after the first minute. Each tank half required the use of 25–50 pounds of molding compound. Only three or four of the tanks were ever made, because testing proved that they cracked under strains similar to those to which they would be subjected in actual use. Although they were not accepted by the Army, because this work proved this particular material unsuitable for jettison tanks of the type desired, it is no reflection upon the quality of the plastic itself, which may be highly successful in other applications. Its adaptability to such large high-pressure moldings, illustrated in Figure 323, is thought-provocative.

Other Furane Resins

Furfural seems destined to play an important role in several types of future plastics. Produced by methods as yet unannounced, "Resin X," a product developed by John Delmonte of the Plastics Industries Technical Institute, is another furane resin of versatile application. The rates of resinification of furfuryl alcohol and furfural in the presence of hydrochloric acid are shown as a function of catalyst concentration in Figure 324.

"Resin X" is a liquid thermosetting resin, indefinitely stable at room temperature. Addition of a catalyst converts it to the solid, cured state. It can be used for casting and laminating purposes and can be molded by impregnation of dry pulp preforms. It may also be applied as a surface coating and as an impregnating agent for porous materials like plaster-of-Paris. Its most significant application thus far has been as an adhesive. For this purpose, it is available in the form of a 100 per cent liquid resin for bonding plastic parts at room temperature. Under the designation "Resin XV," it is produced in 50 per cent solution in organic solvent for use as a hot setting adhesive especially for bonding metal parts.



Courtesy Woodside Industries

Figure 323. Jettison gasoline tanks molded experimentally from rag stock, redwood powder, and Irvington 1226 resin.

(Photograph release approved by Army Air Forces, TSPRO, Wright Field)

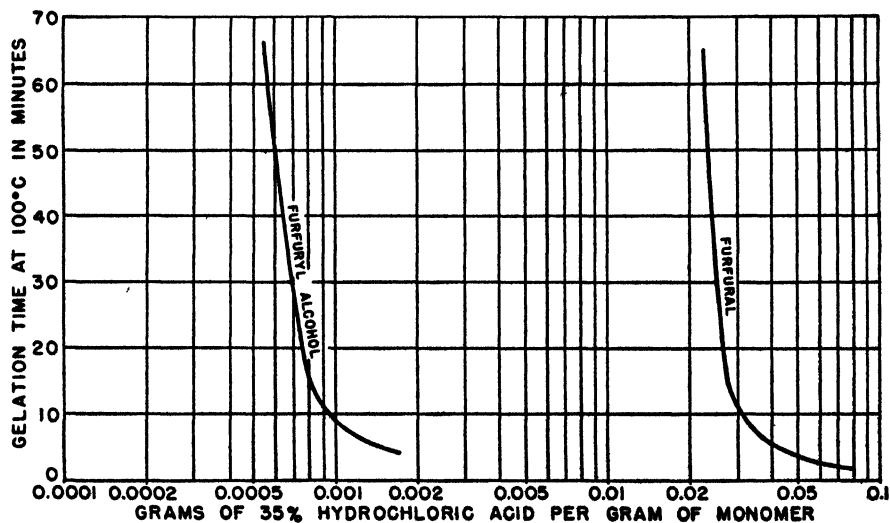


Figure 324. Comparative rate of resinification of furfural and furfuryl alcohol, in the presence of hydrochloric acid, based on approximate time required for gelation. (Delmonle⁸)

It is notoriously difficult to bond together fully cured phenolic laminates. "Resin X," however, can be used as an adhesive for these plastics and unites them so firmly that where a properly cured joint is placed under shear, failure will first occur in the phenolic skin or body of the laminate rather than at the bond or in the adhesive. The shear strength of the bond decreases somewhat with increasing temperature, but joints are resistant to boiling water. Another remarkable feature of "Resin X" bonds is the fact that their strength is relatively independent of the thickness of the glue line, joints having been prepared with glue lines up to 1/32 inch in thickness wherein the laminated phenolics so united failed before the adhesion or adhesive. Thoroughly satisfactory bonds between phenolic laminates are made from "Resin X" by adding catalyst and curing overnight at 120° F or for several days at 85° F.

Other materials which can be united with "Resin X" include "Marco" and "Laminac" laminates, compregnated wood (after sanding), synthetic rubbers, natural rubber (after cyclizing with sulfuric acid), aluminum, brass, and ceramic materials.

Physical properties of cast "Resin X" are listed in Table 187.

Table 187. Properties of "Resin X"*

Tensile strength (ultimate)	4,000 lb/sq in
Compressive strength	12,000 "
Flexural strength	9,000 "
Modulus of elasticity (flexure)	1,100,000 "
Shear strength (Johnson shear tool)	5,700 "
Water absorption (24 hr)	0.05%

Military applications of "Resin X" have included the bonding of synthetic rubber to phenolics in valve assemblies, cementing of ammunition boxes, and bonding of aircraft flooring.

Newcomers to the ranks of furfural resins are "Duralon" and a related material sold for surface coating applications under the trade name, "Tygon F-460." While the specific nature of these two products has not been divulged, they appear to be obtained from furfuryl alcohol by the action of acids. Early products of this type were derived, in part, from interaction of furfuryl alcohol and ethyl silicate. Principal applications of these materials to date have been in the field of protective coatings, impregnants, and laminating and casting resins.

"Duralon" 4 and "Duralon" 1 are available as 100 per cent furane resins, being dark colored, viscous liquids which, upon admixture with catalysts such as phosphoric acid, hydrochloric acid, organic sulfonic acids, acetyl chloride, benzoyl chloride, or acidic salts, are capable of being cured to a thermoset product resistant to water, solvents, and

heat. Where concentrations of catalyst in the order of 1 per cent are used, heating to 175–260° F effects cure after several hours, an intermediate rubbery mass being formed before complete conversion to a hard tridimensional product. Thoroughly cured "Duralon" shows a Rockwell hardness of 100–115 on the M scale. It does not cold flow and does not support combustion. It can be easily machined. Its resistance to dilute acids and alkalies at room temperature is good, but it is not stable in the presence of oxidizing acids and should not be used in contact with concentrated alkalies. It is said to be highly resistant to organic solvents, water, and water vapor. Top operating temperatures range from 325 to 375° F. It possesses interesting electrical properties, being non-tracking and having a breakdown voltage in excess of 1000 volts per mil.

Uncured "Duralon" may be dissolved in such solvents as ketones, esters, and aromatic hydrocarbons. It may also be blended with certain other synthetic resins such as oil-modified phenolics, alkyds, coumarone-indene resins, and drying oils.

For a more detailed discussion of furane resin adhesives, see John Delmonte, "Chemistry and Technology of Adhesives," New York, Reinhold Publishing Corp., In press.

KETONE RESINS

Various ketones can be resinified either as a result of enolization and polymerization of the unsaturated isomer, or by polymerization of an unsaturated ketone produced by intermediate reaction with formaldehyde and subsequent dehydration.

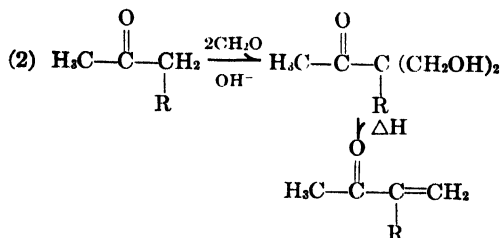
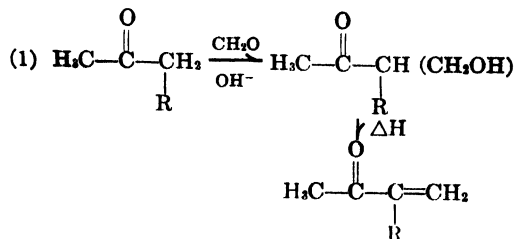
Cyclohexanone Resins

Soluble varnish resins can be made from cyclohexanone by condensation with either acids or alkalies at elevated temperatures. This ketone may also be resinified by condensation with formaldehyde. Numerous other resinous bodies have been produced experimentally from cyclohexanone. It has been rumored that American production of cyclohexanone resins is scheduled for the near future.

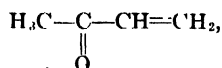
Polymers of Alkyl Vinyl Ketones

Considerable study has been made of the condensation of aliphatic ketones with formaldehyde to obtain polymerizable monomers. Most attention has been directed to acetone and methyl ethyl ketone. Resins from the latter compound appear more promising than those derived from acetone. Although the course of reaction can be controlled to yield numerous products, the most useful monomers produced from these sub-

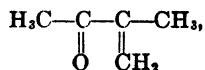
stances are the corresponding vinyl ketones, obtained according to equations (1) and (2), where R is H or CH₃.



The unsaturated compounds, methyl vinyl ketone,



and methyl isopropenyl ketone,



boil at 80 and 98°, respectively. They polymerize spontaneously on standing—more rapidly upon heating or treating with peroxide catalysts—to colorless transparent plastics. The products may develop a yellow or faint greenish shade upon standing for several months. The resins are soluble in ketones and esters, but insoluble in water, ether, alcohols, and hydrocarbons. The polymeric substance obtained from methyl vinyl ketone possesses a refractive index of 1.50 and softens between 50 and 60°. Properties of polymeric methyl isopropenyl ketone, derived from MEK (methyl ethyl ketone), are listed in Table 188.

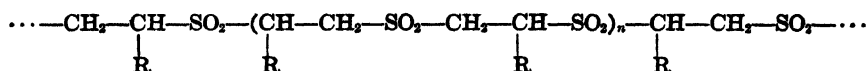
These resins have been proposed as molding powders, adhesives, and impregnating compositions. Sir Gilbert Morgan and his coworkers at the Chemical Research Laboratory, Teddington, England, and the du Pont Company in this country have carried out extensive investigations of vinyl ketone polymers, but as yet no industrial products of the kind are on the market, although monomeric methyl vinyl ketone has recently been made available by du Pont.

Table 188. Certain Physical Properties of Polymethylisopropenyl Ketone²⁰

<i>General</i>	
Specific gravity at 20°	1.11–1.15
Brinell hardness	About 20
Softening range	60–80°
Water absorption, % by weight	
After 24 hr at 20°	0.3
After 7 days at 20°	0.7
<i>Optical</i>	
Refractive index, n_D	1.5212
Relative dispersion	53.2
<i>Solubility</i>	
Acetone	Soluble
Dioxane	Slightly soluble
Pyridine	Slightly soluble
Alcohol	Insoluble
Benzene	Insoluble

SULFUR DIOXIDE-OLEFIN RESINS—POLYSULFONES

In recent years, considerable interest has been aroused in the production of resinous materials from the reaction of sulfur dioxide with olefins and other unsaturates. Many compounds containing one or more double bonds, including olefins, diolefins, acetylenes, and unsaturated alcohols, ethers, acids, and cyanides, have been found to react with sulfur dioxide to yield polymeric sulfones. The structure of the product varies with the reactants, but Marvel and his coworkers have shown that where olefins of the general formula $R-CH=H_2$ are involved, the resulting polymer is composed of a "head-to-head-tail-to-tail" arrangement of its units, *i.e.*:



Polymers of molecular weights as high as 280,000 have been reported.

As a rule, sulfur dioxide does not react with olefins in the dark in the absence of catalysts, but both light of wave lengths shorter than 3000 Å and a variety of catalysts bring about reaction. Oxygen and numerous peroxides serve as catalysts for this resinification, but their activity declines rapidly, probably as the result of oxidation of sulfur dioxide to the trioxide with consequent diminution of catalyst concentration. Milder oxidizing agents are therefore more effective catalysts. Nitrates which are soluble in the reaction mixture are especially useful. Silver nitrate is particularly active, as little as 0.006 per cent causing 65 per cent conversion of butene-2 to polysulfone in five hours at room temperature, or 100 per cent conversion in forty hours. Such organo-metallic compounds as lead tetraethyl, triphenyl bismuthine, and di-*n*-butyl mercury also act as slow catalysts. Resinification is inhibited by

typical antioxidants and by the presence of such olefins as isobutene, even though this olefin in the pure state forms polysulfones.

In some instances, at least, there appear to be what Frey has called "ceiling temperatures" above which resinification does not occur. In the case of isobutene, for example, reaction occurs readily at 4° and below. It becomes virtually non-existent at about 9°, and does not take place at all at room temperature.

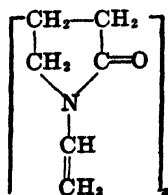
Resinous polysulfones derived from olefins are thermoplastic in nature and can be molded to coherent shapes. That obtained from *n*-butene, for example, can be molded under pressure at 125° to 180°, while the propylene resin requires somewhat higher temperatures in the range of 180° to 200°. Some of the molded plastics are colorless and transparent, but they usually possess more or less color and darken on heating, possibly because of the effect of traces of sulfur trioxide formed during polymerization. The resins vary in solubility characteristics. They are resistant to dilute acids, but are soluble without decomposition in concentrated nitric and sulfuric acids from which they can be precipitated again by dilution. They are decomposed by concentrated alkalis at elevated temperatures. Properties of various molded polysulfones are listed in Table 189.

Potentially, olefin-sulfur dioxide resins are extremely inexpensive. Unfortunately they possess various unfavorable properties, including a tendency toward discoloration and a propensity for gradual depolymerization to sulfur dioxide and the original olefin—characteristics which become especially pronounced upon heating. These drawbacks have thus far precluded commercial development. Extensive study of the industrial possibilities of these products has been carried out by the Phillips Petroleum Company and by the Virginia Smelting Company, the latter in co-operation with Battelle Memorial Institute.

MISCELLANEOUS GERMAN WARTIME DEVELOPMENTS

During World War II, several other classes of resinous materials were developed in Germany on a more or less limited scale.

Polyvinylpyrrolidone,



was produced from γ -butyrolactone, ammonia, and acetylene. This substance, soluble in both water and organic solvents, resembles albumin

Table 189. Properties of Molded Polysulfones *

	Specific Gravity	Tensile Strength (lb./sq. in.)	Compressive Strength (lb./sq. in.)	Transverse Strength (lb./sq. in.)	Impact Strength (ft. lb. for an in. sq.)	Dielectric Strength (Instantaneous) per mil Thickness, Volts	Hardness Brinell No.	Moisture Absorption in 48 hr (%)
Propylene	1.49-1.51	2000-3200	20,400-23,650	2000-6000	1.43-1.72	338-381	40	0.303-0.285
Propylene	—	3200-3685	—	4100-6720	1.84-1.96	—	—	—
Propylene	—	1800-3950	—	5285	—	—	—	—
Propylene	—	1800-2575	—	5380	—	—	—	—
2 parts SO ₂ to 1 propylene	—	3486	—	5380-5475	—	—	—	—
5 parts SO ₂ to 1 propylene	—	3733	—	4080-6195	1.42-1.76	—	—	—
10 parts SO ₂ to 1 propylene	—	3343	—	6000-7150	—	—	—	—
92 % propylene, 8 % 1-butene	—	3780-4300	23,400-24,260	7100-7980	1.50-1.82	—	—	—
84 % propylene, 16 % 1-butene	—	3620-4260	21,260-21,850	6570-8450	1.43-1.83	369-393	—	0.379-0.297
75 % propylene, 25 % 1-butene	—	5615	22,160-23,100	—	—	347-381	—	0.347-0.378
55 % propylene, 50 % 1-butene	—	5929	{ 14,850-18,350 } { 11,850-17,350 }	7210-8050	1.68-1.79	—	—	—
87.5 % propylene, 12.5 % 2-butene	—	4330-4415	22,400-22,650	5910-7000	1.74-1.98	—	—	—
75 % propylene, 25 % 2-butene	—	3820-4080	21,850-22,400	4900-6200	1.77-1.82	372-417	—	0.357-0.372
59 % propylene, 50 % 2-butene	—	4070-4200	19,350-19,850	4800-6000	1.73-1.77	361-401	—	0.477-0.490
75 % propylene, 25 % isobutylene	—	3360-4370	22,850-24,350	6530-6730	1.49-1.81	—	—	—
75 % propylene, 25 % 1-pentene	—	2792-3715	12,350-12,850	3650-4960	1.87-1.94	—	—	—
50 % propylene, 50 % 1-pentene	—	2800-3820	12,350-18,350	4235-5708	1.79-1.98	—	—	—
Mixed preformed resin (25 % butene, 75 % propylene)	—	2465	—	—	—	—	—	—
2-Butene	1.30-1.36	2800-4200	16,850-20,550	5135-5529	1.47-1.73	340-358	25-30	0.695-0.748
3-Butene	—	3100-4000	—	4730-6025	1.69-1.83	—	—	—
2-Butene	—	2300-4460	—	4945-5150	—	—	—	—
50 % 2-butene, 50 % 1-butene	—	3820	15,600	4730	1.85	—	—	—
1-Butene	1.35-1.40	3200-4100	12,950-16,350	4800-6000	1.14-1.18	320-360	20-23	0.371-0.398
1-Butene	—	3113	—	4100-4266	—	—	—	—
1-Butene from n-butyl chloride	—	4298	—	—	—	—	—	—
Allyl alcohol	—	2400-4100	—	3745-7050	1.16-1.28	—	35-49	—
Allyl alcohol	—	2255	—	—	—	—	—	—
1-Pentene	1.31	2100-2350	12,350-13,350	3800-4300	0.665-1.26	355-369	18-19	0.315-0.345
1-Pentene	—	2100-3190	12,350-15,350	3190-4295	0.95-1.32	—	—	—
1-Pentene	—	—	—	—	1.12-1.20	—	—	—
1-Pentene	—	—	12,350-15,100	4600-6280	1.09-1.11	—	—	—
Treated refinery butene	—	3200-3450	—	3550-4375	—	—	—	—
Acid-regenerated refinery butene	—	3330-3955	—	—	—	—	—	—
1-Pentene (with paper pulp filler)	—	6408	—	—	3.94	—	—	—
Mixed butene (with paper pulp filler)	—	5500	—	—	4.57	—	—	—

in physical properties and was utilized during the war in 2.5 per cent aqueous solution as a blood substitute called "Periston." It was used in the treatment of shock, more than 300,000 units having been administered to military personnel.

Polymers of vinyl benzoate were introduced also, but did not meet with much success.

Polyurethanes were among the most important German wartime developments in the plastics industry. They were produced by the reaction of diisocyanates with polyhydric alcohols and were utilized in compression and injection molding powders, as well as in textile fibers and bristles and in leather substitutes. The most important resin of this category, "Igamid," was a linear polymer made by reaction of 1,6-hexamethylene diisocyanate with butanediol-1,4. It was considered equal to nylon in many respects and superior to it in water-resistance and dyeing characteristics.

Other plastics of an entirely different category, belonging to the melamine family, were produced by reacting benzonitrile with dicyandiamide and condensing the product with formaldehyde. Lacquers based on these resins are said to have exhibited better gloss and better heat-resistance than straight melamine types.

COLD MOLDED PLASTICS

The so-called cold-molded plastics were first manufactured in this country in 1908 and enjoyed considerable popularity for over a decade. Although still important in the manufacture of many parts where heat and electrical insulation, as well as resistance to high temperatures, are essential, cold-molded plastics have been greatly out-distanced by hot-molded materials produced from synthetic and semi-synthetic resins developed since 1908.

Cold-molded plastics do not constitute a chemical family. They are usually produced from complex mixtures of miscellaneous binders and fillers and should scarcely be considered in a text dealing primarily with the chemistry of high polymers were it not for the fact that they compete with synthetic and semi-synthetic plastics in fields where heat and electrical resistance are of prime significance.

Cold-molded plastics are composed in large part of inorganic fillers, usually fibrous asbestos with or without other mineral materials such as clay, silica, talc, or barytes, formed into a coherent whole by means of a binder which usually constitutes only one-third to one-sixth of the entire mass. The binder may be inorganic, in which case the product is refractory, or it may be organic in nature.

The prepared batch of material, pulverized, is molded under pressure,

but without heat, in relatively inexpensive molds. Metal inserts are difficult to use in conjunction with cold-molded plastics and greater care is required in ejection of molded articles than in the case of hot-molded plastics. More liberal taper of the mold is essential, for cold-molded materials are fragile before baking. The die used for cold-molded articles usually possesses but a single cavity and the ejected shapes, formed rapidly, are subsequently heated to develop strength. Baking times may last from a few hours to several days, the oven temperature being raised gradually throughout the process until 220° or higher is attained.

With refractory type cold-molded plastics inorganic binders are used. They usually consist of mixtures of hydrated lime and silica and require steam to convert them to a silica-lime cement. Varying from gray to white in color, inorganic, refractory, cold-molded plastics are extremely resistant to heat. They may often be operated continuously at temperatures as high as 1000° F. The line of demarcation between these materials and ceramic bodies is fine, indeed.

Organic binders used for other types of cold-molded plastics are usually bituminous in nature. In some instances they may be based on synthetic or semi-synthetic resins, especially the phenolics. Bituminous binders are largely asphaltic in nature, Gilsonite being often preferred. Pitches, such as stearin pitch or vegetable oil pitches, may also be used and drying oils, as well as rosin and other miscellaneous substances like sulfur, are frequently employed.

In preparing organic compositions of either bituminous or phenolic type, a solvent is employed to facilitate mixing with the binder. This liquid is later allowed to evaporate by aging and its elimination is completed during subsequent baking operations.

Bituminous cold-molded plastics are black or dark gray in color, whereas those bonded with phenolic resins border on brown. Inasmuch as the filler-to-binder ratio is usually in the order of 4:1, the heat resistance of organic-bonded cold-molded plastics is good. In general, however, what is gained in heat resistance is sacrificed in tensile and impact strengths.

Powders for fabrication into cold-molded plastics are usually manufactured by the makers of the finished articles. These materials are available commercially under a variety of trade names from several manufacturers, including the American Insulator Corporation, General Electric Company, Richardson Company, Garfield Manufacturing Company, American Hard Rubber Company, Cutter-Hammer, Inc., Standard Plastics Corporation, Colt's Patent Fire Arms Manufacturing Company, Rostone Corp., and others.

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Conclusion

The story of plastics does not end. To it there is no conclusion. Daily a new resin is born, a striking application created, or a novel process of fabrication perfected. Of this industry Tennyson might well have written: "The old order changeth, yielding place to new."

The most remarkable characteristic of the plastics industry is the versatility of its products. It is this factor which has caught the fancy of the engineer, the manufacturer, and the consumer. Yet not a single plastic possesses properties previously unknown to man. The merit of these materials lies not in their properties *per se*, but rather in the new and unusual ways in which several properties may be combined. Thus the methacrylates are simultaneously shatter-resistant and transparent, some of the synthetic elastomers are rubberlike and yet highly resistant to solvents or oxidation, polyethylene possesses extraordinary dielectric characteristics and can be readily molded into relatively low-cost shapes, silicone fluids show exceptionally low sensitivity of viscosity to temperature. Innumerable other examples of plastics possessing unique combinations of properties are to be found in this text. Indeed, to justify their permanent existence, synthetic resins and plastics must usually have combinations of properties not found in natural materials. They can then do work which other previously available substances could not perform and they become constructional or engineering materials in their own right—not substitutes. And in the development of engineering applications of its products lies the future of the plastics industry!

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